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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

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TITLE OF THE INVENTION (500 characters max)

Thin-Layer Porous Optical Interferometric Sensors for Gases and Other Fluids

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Respectfully submitted,

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USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

Provisional Patent Application

Michael L. Myrick, Paul G. Miney, and Maria V. Schiza
University of South Carolina

Thin-layer Porous Optical Interferometric Sensors for Gases and Other Fluids

We claim the invention having the embodiments described herein.

Abstract

Non-Enabling Abstract

A new type of gas sensor has been designed, constructed and characterized. This sensor uses optical interferents in a porous thin film cell to measure the refractive index of the pore medium. As the medium within the pores changes, spectral variations can be detected. For example, as the pores are filled with a solution, the characteristic peaks exhibit a spectral shift in one direction. Conversely, when tiny amounts of gas are produced, the peaks shift in the opposite direction. This can be used to measure gas evolution, humidity and has potential applications for other interferometric-based sensing devices.

Full Paper

A New Optically Reflective Thin Layer Electrode (ORTLE) Window: Gold on a Thin Porous Alumina Film Used to Observe the Onset of Water Reduction

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Abstract

The fabrication and unique characteristics of a new type of thin layer electrode, an optically reflective thin layer electrode (ORTLE), are described. The electrode was fabricated by the anodization of a thin layer of aluminum sputtered onto a plain glass microscope slide to create a 750 nm-thick porous alumina film. A thin film of gold was then sputtered atop the porous and transparent alumina film. The gold layer remained porous to allow solution into the pores but was optically thick and reflective. Reflectance measurements made through the microscope slide did not interrogate the bulk solution, but show spectral features that shift with the optical properties of the material filling the pores of the alumina film. A simple series of experiments, in which the potential of the ORTLE was stepped negatively to various values in an aqueous sodium sulfate solution shows that interference fringes shift measurably in the ORTLE spectrum at potentials several hundred millivolts positive of the potential at which gas evolution was visible to the naked eye.

Keywords: OTTLE, Porous alumina, Spectroelectrochemistry, Specular reflectance spectroscopy

1. Introduction

Spectroelectrochemistry is a combination of electrochemical and spectroscopic techniques in which optical measurements are referred to the potential of a working electrode. Thin-layer spectroelectrochemistry is possibly the simplest type of spectroelectrochemistry and has advantages such as rapid and exhaustive electrolysis and small volume features [1]. Since the first report in 1967 [2], optically transparent thin layer electrodes (OTTLEs) have been used for such thin layer studies [3–5]. A typical application of an OTTLE is the spectroscopic study of redox processes [6–8]. Various spectroscopic techniques such as luminescence spectroscopy [6], FTIR difference spectroscopy [9] and UV/vis/NIR [10–12] have been coupled with electrochemical techniques via OTTLEs and a variety of OTTLE designs for many purposes have been developed [13–15].

As a consequence of our work with nanoelectrode arrays [16, 17] we have carried out studies into the anodization of aluminum thin films on various substrates. We recently reported a study of the anodization of aluminum thin films sputtered onto an electrically insulating substrate – a plain float glass microscope slide [18]. The resulting porous aluminum oxide (alumina) films are transparent and contain pores varying from approximately 80 to 100 nm in diameter. In this article, we describe the design and characterization of a new type of thin layer electrode which is a variation on the concept of an OTTLE. The essential difference between an OTTLE and our new electrode is that reflectance is collected instead of transmittance. For this reason, the electrode is called an optically reflective thin layer electrode (ORTLE) in the following discussion. This new electrode is based on the porous alumina thin films in [18]. In the case of the ORTLE, spectroscopy interrogates a solution phase within the pores of the alumina film between the electrode face and a window behind it. The electrode is created by thin-film deposition of gold onto the exposed face of the porous alumina, creating a gold electrode filled with holes having a diameter much less than the wavelength of visible light. The thickness of the alumina film – and thus the depth of the pores – can be altered by controlling the thickness of the original aluminum film. Through the use of a combination of specular reflectance spectroscopy and chronoamperometry, we can confine our spectroelectrochemical study to that solution contained within the pores. The ORTLE described here interrogates the thinnest sample of which the authors are aware and is the first based on porous alumina. In this report, we describe the preparation of the ORTLE in detail, plus how the ORTLE is incorporated into spectroscopic measurements. We also characterize the stability of the ORTLE spectrum and its origin, and show how an applied potential affects the observed spectrum in a simple solution.

  DOI: 10.1002/elan.200302926

2. Experimental

2.1. ORTLE Design and Concept

The design of tbe ORTLE is sbown in Figure 1A. A 500 nm aluminum film was sputtered onto a plain float glass slide (75 × 25 × 0.5 mm), anodized and subsequently converted to porous alumina as described previously [18, 19]. The resulting 750 nm thick transparent alumina film was subsequently coated for 210 s with gold using a CRC-100 sputtering system (Plasma Sciences Inc., Lorton, VA), producing a gold film approximately 100 nm thick. Although this appears to be an optically thick gold film, scanning electron microscopy (SEM) studies in our laboratory have shown this is insufficient to seal tbe somewhat larger pores of a commercial porous alumina membrane [16, 17]. The SEM image in Figure 1B shows that tbe pores of the alumina films created by the process in [18] also remain open when coated with gold in tbis way.

The gold film possesses a mirror finish on its "face", the exposed side opposite tbe porous alumina. Despite tbis and the apparent continuity of the film, it is highly porous and allows the filling of the channels in the underlying alumina when exposed to solution. The reverse side of the gold film, however, does not sbow this highly reflective finish, although it presents a mostly specular surface. Light can pass tbrough the optically transparent glass slide used as a support and through the fluid-filled alumina, but is reflected by the porous metal overlayer. Wben a potential is applied to tbe gold film, any solution cbanges tbat occur witbin tbe pores can be monitored by specular reflectance spectroscopy. Note that the ORTLE design requires no special auxiliary or reference electrodes and no special electrode configurations. In our spectroelectrocbemical cell design, we use it as a window into a bulk solution, since only the solution in tbe alumina pores is interrogated.

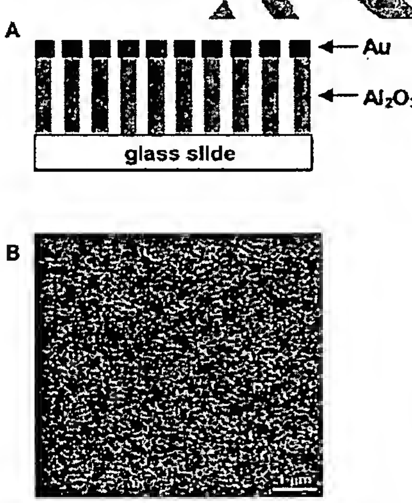

Fig. 1. A) Schematic of the side profile of the ORTLE and (B) SEM image of the porous alumina covered with the layer of gold showing that the pores are not sealed.

2.2. Spectroelectrochemical Cell Design and Set-Up

The ORTLE was mounted in a home built spectroelectrochemical cell (see Figure 2). The cell was constructed from Teflon and contained a rectangular window (75 × 25 × 0.5 mm) to whicb the thin layer electrode could be attached. The ORTLE was positioned with tbe gold sputtered side facing inwards and was beld in place by 8 screws, which could be tightened to avoid any leaking of the solution. The ORTLE subsequently acted as tbe working electrode in the spectroelectrochemical cell. The cell was then mounted on an aluminum base, which could be placed inside the spectrometer. The heigbt of this aluminum base was designed to place the ORTLE in the patb of the incident light beam. Wben tbe ORTLE was attacbed, tbe spectroelectrochemical cell could then be filled witb tbe desired solution, into whicb the auxiliary electrode (PT gauze) and reference electrode (Ag/AgCl/sat. NaCl, BAS, West LaFayette, IN) could be inserted.

The home built spectroelectrochemical cell was placed inside a goniospectroreflectance attacbment (750–75 MA, Optronic Laboratories Inc., Orlando, FL) as sbown in the schematic of Figure 3. It was then illuminated by a tungsten quartz-balogen lamp (150 W) and monochromator (750 M-S, Optronic Laboratories Inc.) combination that selected

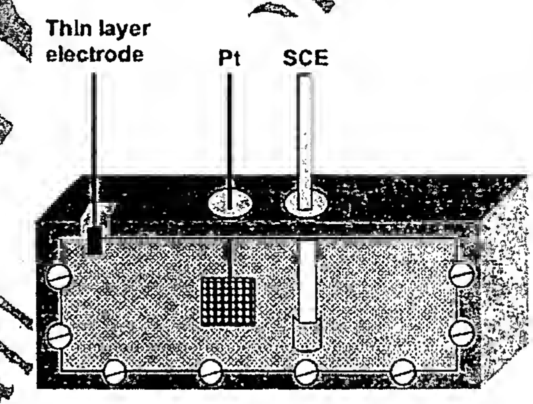

Fig. 2. Schematic of the spectroelectrochemical cell in which the ORTLE is mounted.

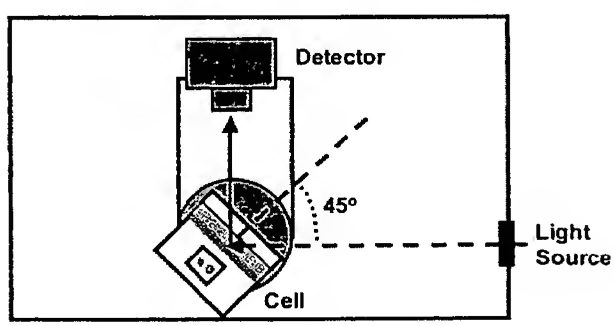

Fig. 3. Schematic of the cell in the spectroelectrochemical set-up.

wavelengths in the range of 280–1100 nm. A silicon detector (DH-300EC, OL750-HSD-301EC, Optronic Laboratories Inc.) was used to record the reflected intensity. The spectra were obtained by the Optronic Laboratories software and further analyzed using IGOR Pro (Version 4.01, Wavemetrics, Inc.).

All electrochemical experiments were carried out using an EG&G PARC Model 263 potentiostat, connected with a general purpose interface bus (GPIB) (National Instruments, Atlanta, GA) to a Gateway 2000 Model P5-60 computer with EG&G Model 270 Research Electrochemistry Powersuite Software. Gold wire electrodes were purchased from CH Instruments, Austin, TX. Potassium ferricyanide (Mallinckrodt, Hazelwood, MO) and sodium sulfate (Fisher Scientific, Suwanee, GA) were all reagent grade and were used without further purification. All solutions were prepared with deionized water. SEM images were collected using a Quanta 200 scanning electron microscope (FEI Company, Hillsboro, OR).

3. Results and Discussion

3.1. Characterization of the ORTLE

Figure 4 shows how the ORTLE functions as a typical working electrode. In this figure, a comparison is made between a cyclic voltammogram (CV) obtained at a conventional gold wire electrode (A) and one obtained using the ORTLE as a working electrode (B). Both experiments were carried out in 0.01 M ferricyanide/0.05 M sodium sulfate solutions at 20 mV s^{-1}. As can be seen in Figure 4, the ORTLE behaves similarly to the wire electrode. The purely electrochemical characteristics of the ORTLE electrode reflect those of bulk solution conditions because the electrode is immersed in bulk solution. What is important to take from this experiment is the ability of the ORTLE to exhibit the standard characteristics that would be expected in a ferricyanide solution, given that the design of the electrode is such that a very thin gold layer is sputtered on a porous alumina film and does not seal the pores.

A decrease in the separation of the peaks was observed for the ORTLE, which would be expected for a contribution from restricted diffusion occurring within the pores. To test this, an experiment was conducted to measure the effect of sweep rate (ν) on the peak current. For a thin layer cell, the peak current should be directly proportional to ν [13, 20]. This study revealed a poor relationship between peak current and ν and an excellent relationship between peak current and $\nu^{1/2}$ ($R^2 = 0.999$). This result indicates that, for this CV, the contribution of thin layer electrochemistry is negligible compared to that of the bulk solution.

Figure 5 shows transmittance spectra of a plain float glass microscope slide (A), of a similar glass slide with a layer of porous alumina (B), and of an ORTLE (C), all taken at a 45° angle to the incident beam. Interference effects in the spectrum (B) are the result of the refractive index contrast between glass and the overlying films, while the reduced overall transmittance is due to the absorbance of residual aluminum in the film and scattering in the film. The transmittance of the ORTLE is negligible on the scale of Figure 5 due to the presence of the reflective gold film and thus little interrogation of the bulk solution can occur through the film. Spectroscopic changes based on specular reflectance on the backside of the gold film must therefore be ascribed to either changes in the medium within the pores or changes in the electrode itself.

Figure 6 shows a typical specular reflectance spectrum (solid black line) obtained for the ORTLE without any solution in the cell. The specular reflectance measurements were performed by positioning the cell at 45° to the incident beam, and the detector at 90° to the specular reflected beam (see Figure 3). Single-beam reflectance measurements were referenced to the total intensity of the source by directing 100% of the incident beam to the detector before each experiment. Several small interference peaks can be observed at shorter wavelengths with a relatively large peak usually observed within the range of approximately 700–1000 nm (the wavelengths and the appearance of the peaks varied from ORTLE to ORTLE due to slight differences in the thickness of the original aluminum films). Upon the introduction of a sodium sulfate solution, the peaks shifted

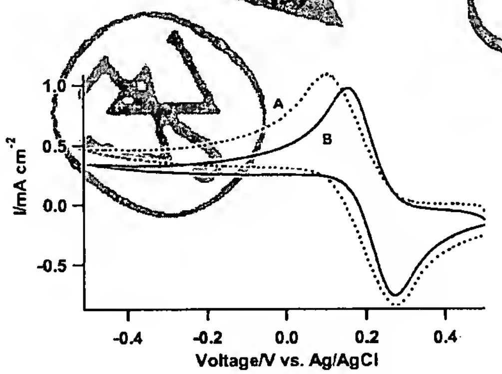

Fig. 4. CVs, carried out at 20 mV s^{-1} in a 0.01 M potassium ferricyanide/0.05 M sodium sulfate solution, obtained for a standard gold electrode (A) and the ORTLE (B).

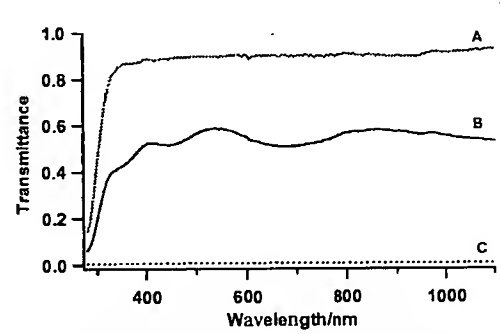

Fig. 5. Transmission spectra for a glass slide (A), a glass slide coated with an alumina layer (B) and the ORTLE (C).

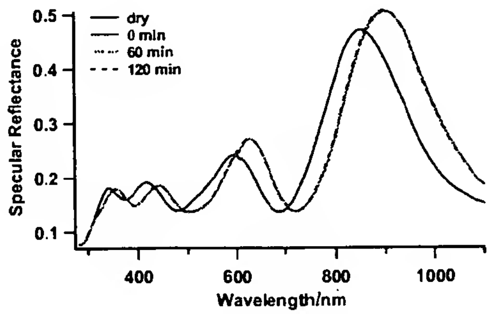

Fig. 6. Specular reflectance spectra showing the red shift observed after the introduction of a 0.05 M sodium sulfate solution, and monitoring the changes in the spectra over time.

towards longer wavelengths, accompanied by an increase in intensity – for this sample the large peak shifted from 850 to 900 nm, as indicated by the spectrum collected after 0 min (i.e., it was collected immediately after the introduction of the sodium sulfate solution). The spectra collected after 60 min and 120 min show, that for this ORTLE, no further red shifts or increases in intensity were observed. While this particular ORTLE responded promptly, some ORTLEs showed a gradual red shift over time after solution was introduced. In all cases, less than 1 hour was necessary for this change to be completed. At least part of this change is likely the result of pores being filled with solution and changing the effective refractive index of the porous film, as the shift is consistent with changes in interference fringe positions expected in that case within a factor of two.

Referring to Figure 7, one condition for the appearance of strong interference-based oscillations in the reflection spectrum of the ORTLE is that the reflectivity of the glass/alumina and alumina/gold interfaces are of comparable magnitudes. This is achieved only because the electrochemical synthesis of the porous alumina film leaves a small amount of aluminum metal behind at the glass/alumina interface, approximately 1.2 nm thickness on average as indicated by ellipsometry [18]. Aluminum is the most

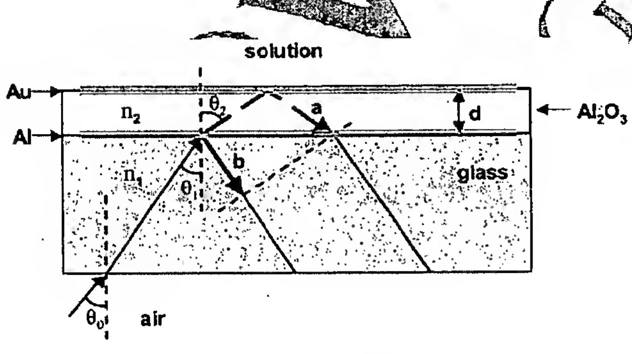

Fig. 7. Schematic of the optical pathlengths (a and b) of incident light from air through the glass substrate (refractive index $= n_1$) and alumina layer (refractive index $= n_2$ and thickness = d) with two reflective interfaces resulting from unanodized aluminum and the gold coating.

opaque metal in the visible region. According to optical modeling of this electrode, too much aluminum at the interface (e.g., 50 nm) would cause the spectrum of the ORTLE to be that of an aluminum mirror. Too little aluminum at the interface would produce a spectrum like that of a gold mirror with small (e.g., 5%) interference oscillations in the blue and UV, dropping to about 1% oscillation in the red and NIR.

With this first condition met, constructive interference in reflection occurs when the difference in the optical pathlengths **a** and **b** are an integral number of wavelengths of incident light. Assuming an isotropic material with no absorbance, the optical pathlength is the physical pathlength multiplied by the (real) refractive index of the medium. Making use of Snell's law:

$$\sin(\theta_0) = n_1 \sin(\theta_1) = n_2 \sin(\theta_2) \tag{1}$$

where θ_0 is the angle of the incident light from air to the glass, θ_1 is the angle that the beam enters the porous alumina layer from the glass substrate, θ_2 is the angle of the beam that interacts with the gold layer and n_1 and n_2 are the refractive indices of the glass and porous alumina layers, respectively.

It is possible to show that the optical path difference (OPD) is:

$$\mathrm{OPD} = 2d\sqrt{n_2^2 - \sin^2(\theta_0)} = m\lambda_{\max} \tag{2}$$

where m is a non-negative integer, d is the film thickness and $\lambda_{\max}$ is the maximum wavelength. The apparent refractive index of the film, n_2, is approximately related to the volumetric composition of the films, assuming the film structure to be heterogeneous on a scale less than the wavelength of light and with no regular repeating patterns.

For the dry film,

$$n_2 \approx n_{Al_2O_3}(1 - f_p) + f_p \tag{3}$$

where $n_{Al_2O_3}$ is the refractive index of alumina, f_p is the pore fraction of the porous alumina and the refractive index of air is taken to be 1. As the pores of the alumina film fill with solution Equation 3 becomes:

$$n_2 \approx n_{Al_2O_3}(1 - f_p) + 1.33 f_p \tag{4}$$

where the refractive index of the filling solution is assumed to be that of water. For any value of m,

$$\frac{\lambda_{\max\,dry}}{\lambda_{\max\,wet}} = \frac{\sqrt{n_{2,dry}^2 - \sin^2(\theta_0)}}{\sqrt{n_{2,wet}^2 - \sin^2(\theta_0)}} \tag{5}$$

Since the refractive index of the solution filled film is always greater than that of the dry film, the filling of the pores will always result in a red shift.

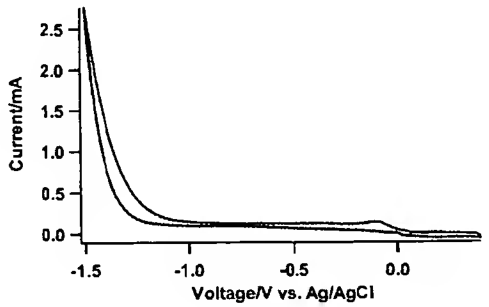

Fig. 8. CV obtained for an ORTLE, carried out at 5 mV s^{-1} in a 0.05 M sodium sulfate solution, showing the background limit of the solution.

3.2. Reduction of Water

In the remainder of this manuscript, we report observations made by specular reflectance spectroscopy on the ORTLE as a function of potential in a simple solution of 0.05 M Na_2SO_4. For these experiments, the auxiliary and reference electrodes were inserted into the spectroelectrochemical cell and the three electrodes were connected to a potentiostat. Figure 8 shows a CV for the Na_2SO_4 solution where the potential was swept from +0.4 V to −1.5 V vs. (Ag/AgCl). The positive potential limit observed for the ORTLE was apparently due to gold oxide formation. More positive potentials resulted in delamination of the fragile gold film from the porous alumina substrate, a common indicator of stress at the film/substrate interface. The negative potential limit of the ORTLE was not due to delamination but apparently to dissolution of the porous alumina by hydroxide ions generated during hydrogen evolution. The cathodic current associated with hydrogen evolution can be seen to begin at approximately −1.1 V (vs. Ag/AgCl) in Figure 8.

The ORTLE for which results are described in Figure 9 show a "dry" reflectance spectrum in which one of the observed peaks was centered at 725 nm. The addition of the sodium sulfate solution to the spectroelectrochemical cell caused this peak to shift to 755 nm. Reflectance spectra were acquired during the 400 s that the potential was held at a certain value for steps to potentials between +0.1 V and −1.2 V (vs. Ag/AgCl). Figure 9A shows detail in the reflectance spectrum of this ORTLE at a subset of these potentials, between −0.4 V and −1.1 V (vs. Ag/AgCl), with the "dry" spectrum for reference.

No significant changes were observed in the ORTLE reflectance spectra at potentials positive of −0.5 V (vs. Ag/AgCl). When the potential was stepped to −0.5 V (vs. Ag/AgCl), however, a blue shift of the peaks was observed. As Figure 9A shows, the interference peak at 755 nm continued to shift toward the blue very gradually with increasing negative potential until −1.0 V. A decrease in intensity was not observed over this potential range; in fact, a slight increase in intensity was observed. When the potential was stepped to −1.1 V, however, a more pronounced blue shift of the large peak at 755 nm was observed that was

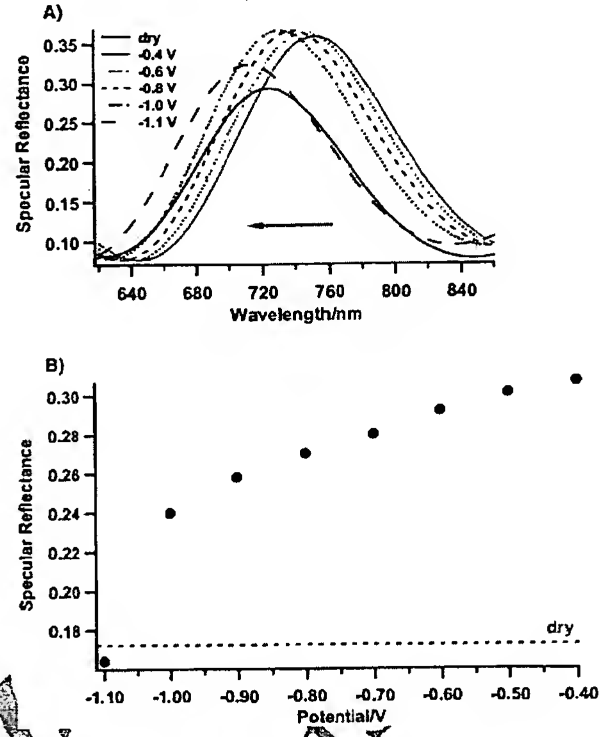

Fig. 9. A) Effect of potential on the specular reflectance spectrum concentrating on the peak at approximately 755 nm and (B) decrease in magnitude of the reflectance at 780 nm with increasing negative potential. The dashed line indicates the dry state of the ORTLE at 780 nm.

accompanied by a substantial decrease in intensity. This is interpreted as the result of gas infiltrating the pores of the alumina. Spectra obtained at more negative potentials showed weaker and broader interference peaks that did not recover when the electrode was returned to more positive potentials. This is interpreted as a result of the concomitant generation of hydroxide during hydrogen evolution; hydroxide is known to dissolve the porous alumina film and could cause collapse of the ORTLE structure. Further experiments are under way at present to test this hypothesis by controlling the pH with a buffer solution.

In electrochemical experiments carried out with ORTLEs outside of the spectrometer, it was not possible to see hydrogen evolution with the naked eye until the potential approached −1.5 V. The increase in current observed in Figure 8 near −1.1 V is, however, attributable to the onset of water reduction. The low level of hydrogen production occurring at −1.1 V was insufficient to form bubbles large enough to be observed by the naked eye, but sufficient to strongly perturb the ORTLE specular reflectance. Assuming pores to be filled initially with water and that this water is displaced by gaseous hydrogen generated at the electrode, the apparent refractive index of the film can be written as:

$$n_2 \approx n_{Al_2O_3}(1-f_p) + 1.33f_p - RTn_{H_2}/(3dA) \quad (6)$$

where n_{H_2} is the number of moles of H_2 produced, A is the area of the electrode, R is the ideal gas constant, and T is the absolute temperature.

Inserting this definition into equation 2, solving for wavelength and taking the derivative with respect to the number of moles of H_2 produced under initial conditions of pores filled with only water or a water-like electrolyte, we obtain:

$$\lambda_{max} = \frac{2d\sqrt{\left(n_{Al_2O_3} - f_p\left(n_{Al_2O_3} - 1.33\right)\right)^2 - \sin^2(\theta_0)}}{m}$$
$$\frac{\partial \lambda_{max}}{\partial n_{H_2}} = -\frac{2RT\left(n_{Al_2O_3} - f_p\left(n_{Al_2O_3} - 1.33\right)\right)}{3mA\sqrt{\left(n_{Al_2O_3} - f_p\left(n_{Al_2O_3} - 1.33\right)\right)^2 - \sin^2(\theta_0)}} \quad (7)$$

Inserting a void fraction of 0.32 (estimated from ellipsometry [18]), a film thickness d of 680 nm (estimated from modeling of the film in Figure 6), and an incident angle of 45 degrees, the maxima should occur at:

$$\lambda_{max} \approx 1851\ \text{nm}/m \quad (8)$$

From Equation 5, it is evident that $m=2$ for the long-wavelength peak in Figure 6, and is 3, 4 and 5 for the peaks at progressively shorter wavelengths. Returning to Equation 4, the sensitivity of the peak position of the $m=2$ peak to hydrogen is:

$$\frac{\partial \lambda_{max}}{\partial n_{H_2}} = -\frac{9\times 10^{10}\text{nm mol}^{-1}\text{cm}^2}{A} \quad (9)$$

Equation 6 indicates that 0.1 nanomole of H_2 produced per centimeter squared area of electrode surface could result in a 9 nanometer hypsochromic shift in the $m=2$ peak. If we assume that a 1 nm shift could be detected, and we imagine our sensor on the end of a fiber-optic with an area of 10^{-4} cm^2, approximately 1 fM of H_2 evolution could be detected if the gas were captured in the pores of the alumina.

Subtle shifts in the wavelength of the interference peak maximum (in Figure 9A were) observed at potentials as positive as -0.5 V (vs. Ag/AgCl). The origin of this shift is unknown at present, but must involve changes in the composition of the porous film or of the solution in the pore volume. The blue shift indicates an overall decrease in the optical thickness of the film under these conditions, an effect that is consistent with displacement of pore solution by nanoscale bubbles. In Figure 9B, the variation in the magnitude of the reflectance at 780 nm is plotted against potential. As can be seen in this figure the intensity follows a similar trend with varying potential, in that a large increase of intensity is observed upon the addition of solution and a gradual decrease observed with increasing negative potential. Eventually, at -1.1 V Figure 9B shows that the intensity is similar to that of the electrode in the dry state.

4. Conclusions

A new type of thin layer electrode, based on a gold-coated porous alumina film, has been designed and fabricated. The cell was characterized by cyclic voltammetry and spectroscopic techniques and by spectroelectrochemistry, where a combination of specular reflectance spectroscopy and chronoamperometry was used. Typical spectra exhibited several strong interference peaks which resulted from the presence of a small amount of unanodized aluminum at the glass/porous alumina interface. A red shift of the peaks in the specular reflectance spectrum and an increase in intensity was observed upon the introduction of a sodium sulfate solution to the spectroelectrochemical cell where the ORTLE was mounted. We believe that this was due to refractive index changes arising from the filling of the pores by the solution. A blue shift of the peaks could be induced by stepping the potential to values increasingly negative of -0.5 V (vs. Ag/AgCl) and towards the background limit of the solution. Upon stepping to -1.1 V, a pronounced blue shift was observed, accompanied by a decrease in intensity. We believe that this is due to the production of hydrogen within the pores of the ORTLE.

Finally, this new electrode differs from typical thin-layer electrodes in several ways. First, no transparent electrodes are required, and the solution does not have to be transparent or even homogeneous, because the nanostructured electrode face filters out particles large enough to cause significant scattering. The electrode can thus be used in bulk solutions as a window that does not allow light into the bulk – similar to total internal reflection techniques, but with no critical angle constraints. Further, the electrode can potentially be designed to combine refractive-index measurements with surface plasmon resonance and UV-visible absorbance measurements with very minor changes.

5. Acknowledgements

The authors gratefully acknowledge the USC NanoCenter and the Petroleum Research Fund (ACS PRF# 36477-AC5) for support of this research.

This effort was also sponsored by the Human Effectiveness Directorate, Air Force Research Laboratory, Air Force Materiel Command, USAF, under grant number F33615-00-2-6059. The U.S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation thereon. The views and conclusions contained herein are those of the authors and should not be interpreted as necessarily representing the official policies or endorsements, either expressed or implied, of the AFRL Human Effectiveness Directorate or the U.S. Government.

We would like to thank Mr. Allen Frye for building the spectroelectrochemical cell.

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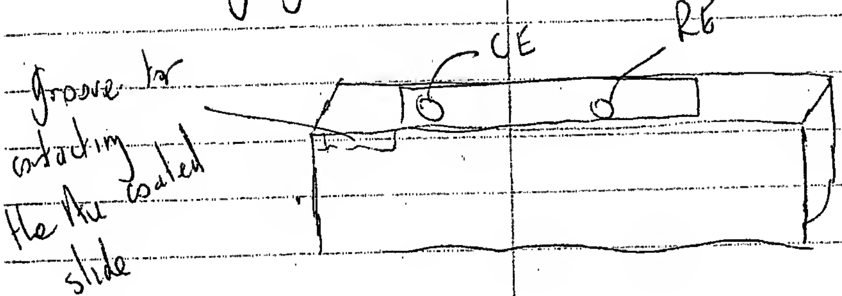
29 May 2003

Design of cell for electroanalysis paper

Going to place Al_2O_3 coated slide horizontally into cell.



-0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6
Potential (V)

June 6 - June 16

Have being anodizing glass slides coated with aluminum

These are full glass slides and are difficult to fully anodize.

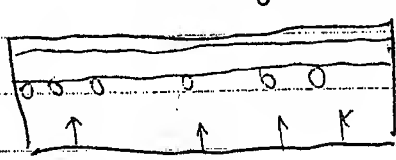
Have anodized many and failed alot of the time.

Have being placing the sides horizontally in solution.

Sucessful anodization occurring @ 60-65V !!
not 80V.

Best results using packing tape and not electroplating tape!!

For electroplating tape, bubbles of gas which form during the anodization congregate at the bottom of the tape. This causes the anodization to occur more rapidly at the top, thereby causing contact to be lost.



Packing tape causes the bubbles to "skim" over the tape.

No stirring also gives better anodization!!

Placing of counter electrode ⊥ to the WE works best!

Potential (V)

Also have been doing work on specular reflectance with Maria for Electroanalysis paper.

Have been doing work in designed cell. For analysis & details of results & expts, check Maria's notebook as she has kept very good, accurate, & through notes!!

June 16: 2003

Carried out ~~expts~~ first spectroelectrochemistry expts with the "OTTLE"!

Used 0.05M Na_2SO_4 as the solution - was not de-aerated as had to insert the solution into the cell with a pipette!

Used Ag/AgCl reference electrode as the RE and the Pt gauze as the CE.

The working electrode was the gold coated, alumina coated glass slide.

Cell takes about 50-55 mls to fill it.

Carried out specular reflectance expts before and after insertion of the solution into the cell. Usual 'red-shift' observed

Carried out a few CV expts to see if the set-up actually worked

ss61603a 0.4V → -0.1V → 0.4V @ 10mV/s
Worked well, a little 'noisy' but not bad at all.

ss61603b 0.4V → -0.3V → +0.4V @ 10mV/s

-0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6
Potential (V)

Again, a good, smooth CV. Stopped at ~~-0.3V~~ -0.2V as cu[rrent]
rose rapidly - did not want excessive hydrogen evolution
result in destruction & delamination of the gold film.

Was trying to find exactly were 'hydrogen evolution' cathodi[c]
current started. Did not want to go too negative.

Idea was to see if H_2 evolution at -ve potentials could [be]
picked up by the specular reflectance technique. What should be
expected is a 'blue shift' of the spectrum ~~to where~~ towards [...]
peaks were observed prior to insertion of solution. This is
as a result of the generation of an 'air like' situation within
pores.

Expts were carried out like this:

Maria's specular reflectance experiments lasted approx 5min ?
335s

I set ~~of t~~ up the potential step expts for 400s. When [the]
intial charging spike was observed, Maria started the specul[ar]
reflectance expt. Always stepped from 0.1V as the CV exp[t]
revealed that no current was evident at this potential.

616 step ~~0~~1 0.1V → 0V

616 step ~~0~~2 0.1V → -0.05V

616 step 3	0.1V	→	-0.1V
616 step 4	0.1V	→	-0.15V
616 step 5	0.1V	→	-0.2V
616 step 6	0.1V	→	-0.25V
616 step 7	0.1V	→	-0.3V
616 step 8	0.1V	→	-0.4V
616 step 9	0.1V	→	-0.5V
616 step a	0.1V	→	-0.6V
616 step b	0.1V	→	-0.7V
616 step c	0.1V	→	-0.8V
616 step d	0.1V	→	-0.9V
616 step e	0.1V	→	-1V
616 step f	0.1V	→	-1.2V

-0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6

Potential (V)

~~Wed~~ Thursday 19/6/03

Carried out similar spectroelectrochemical expts to those carried out on Monday 16/6.

ss61903a   0.4V → -0.1V → -0.4V @ 10mV/s

Good contact and good CV obtained - not much noise.

ss61903b   0.4V → ~~-1.2V~~ -0.4V → -0.4V @ 10mV/s

Potential Step expts.

s619step a   0.1V → -0.1V for 400s.

b   → -0.3V

c   → -0.5V

d   → -0.7V

e   → -0.8V

f   → -0.9V

-0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6
Potential (V)

Friday 20/6/03

Carried out expts with gold coated aluminum films, in normal 3 electrode set up. Wanted to see where hydrogen evolution started i.e. what potential do we see the first bubbles.

Used 0.05 M Na_2SO_4 (undeaerated) and new potentiostat

h2 gold 62003a   0.4V → -1.3V → 0.4V @ 5mV/s

Nothing really observed i.e. no bubbles to the naked eye! 'H_2 peak' was quite prominent.

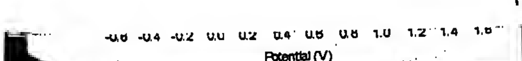
h2 gold 62003b   0.4V → -1.5V → 0.4V @ 5mV/s

Could see small bubbles to the naked eye. Could the changes that ~~my self~~ myself & Maria see in specular reflectance be due to bubble formation in the nano range which would make a huge difference to the spectra in the nano pores - these 'nano h_2 bubbles' would not be observable to the naked eye?

h_2 gold 62003c -- mistake!

h_2 gold 62003d   0V → -1.5V → 0V @ 5mV/s

Wanted to sweep into the O_2 formation region.



Gold oxide stripping peak observed on return ~~cv~~ sweep
Film was damaged from this expt.

h2 gold 620030 0V → -1.5V → +1.5V → 0V @ 5mV/s

Wanted to see the whole range.

Spectroelectrochemistry on Friday

Examining "good" glass slide. in 0.05 M Na_2SO_4

55620039 0.3V → -0.1V → 0.3V @ 10mV/s.

Saw that current was closer to zero @ -0.05V good CV's not much noise. → Started all potential steps from -0.05V

620 step a -0.05V → -0.1V 400s.

620 step b -0.05V → -0.2V

620 step c -0.05V → -0.3V

620 step d -0.05V → -0.4V

620 step e -0.05V → -0.5V.

continuous slight blue shift

Ran a spec rat. expt after 620 step d without any applied potential to see if we could arrest the continuous blue shift - we did not. Irreversible changes from within the film.

-0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6
Potential (V)

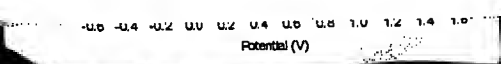
620 step f + 0.05V → - 0.6V

620 step g - 0.05V → - 0.07V.

SS 62003b + 0.4V → - 1.2V → 0.4V @ 10

June 23 - July 1

Wrote paper on the "Onset of water reduction" which was submitted to Electroanalysis. All information is in the paper and can be got from Mo-wi's notebook - ie spectroscopy data.



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05/28/03

- Coating of CaF_2 window

Pinm + B	Set P	W	V	A
	2000W	2000W	526V	3.79A

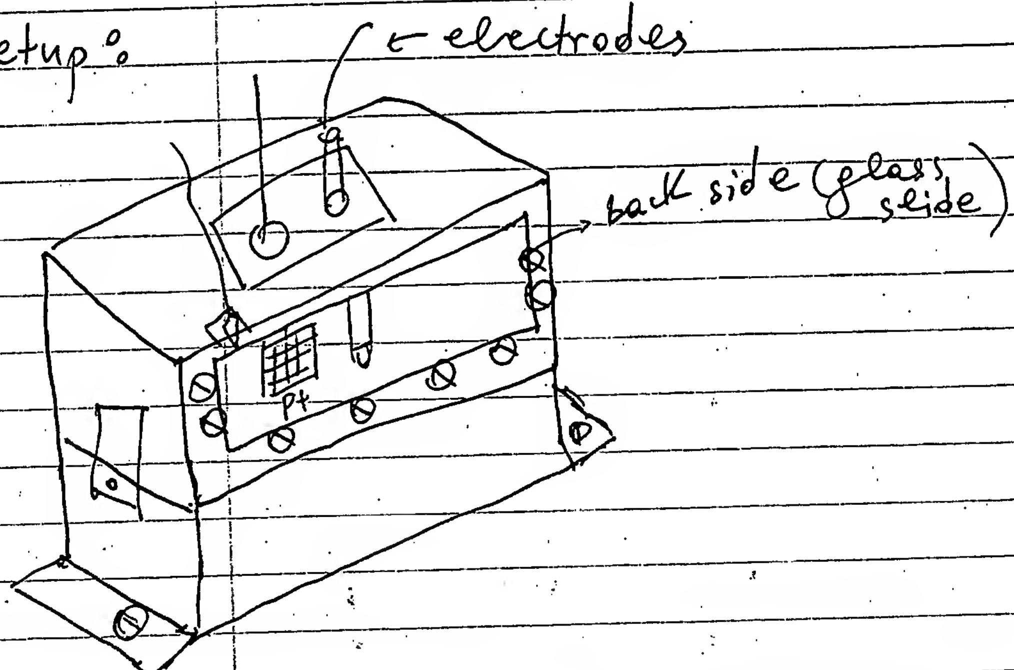
Toggles = 8
thickness = ~500nm (2 × 257nm)

Very nice clear Al coatings.

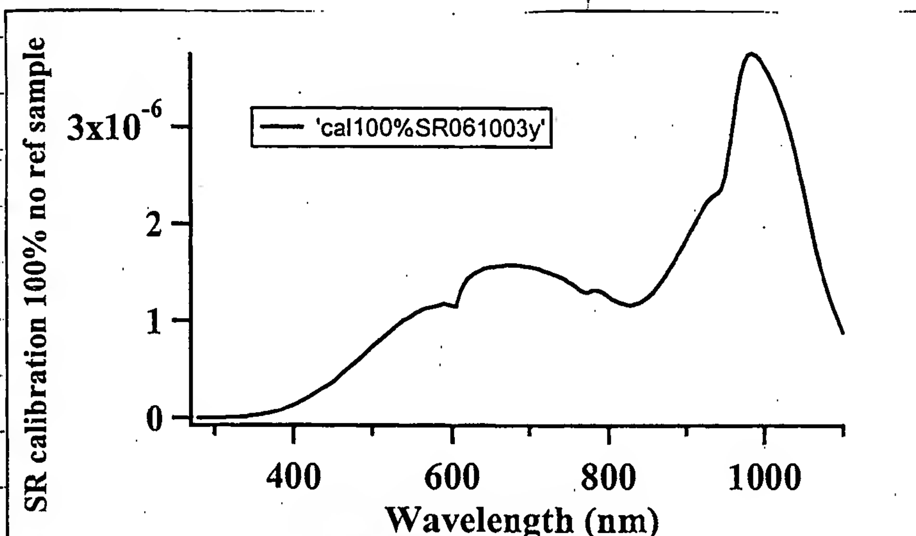
05/29/03 to 06/10/03

Specular Reflectance of Gold-alumina coated slides with 750-75MA attachement
Al → ~500nm → anodized (by Paul) → Gold coated for 3.5 min with sputterer in GSRC.

Cell setup:

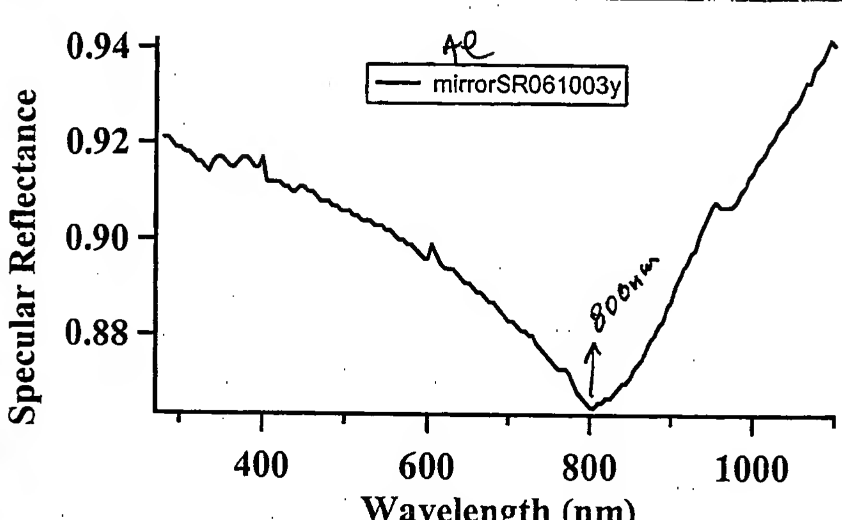


06/10/03

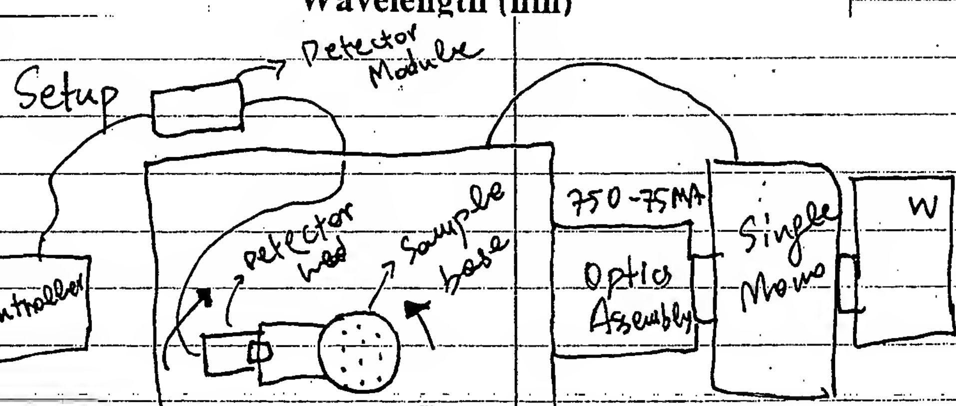


Calibration after alignment procedure (follow the manual)

With no reference sample

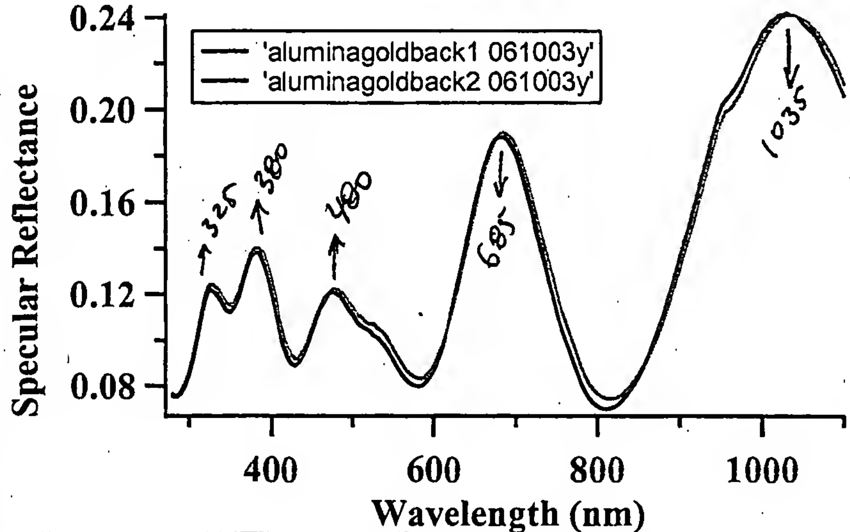


Al ~ 50nm
SR
Minimum reflectivity at 800nm

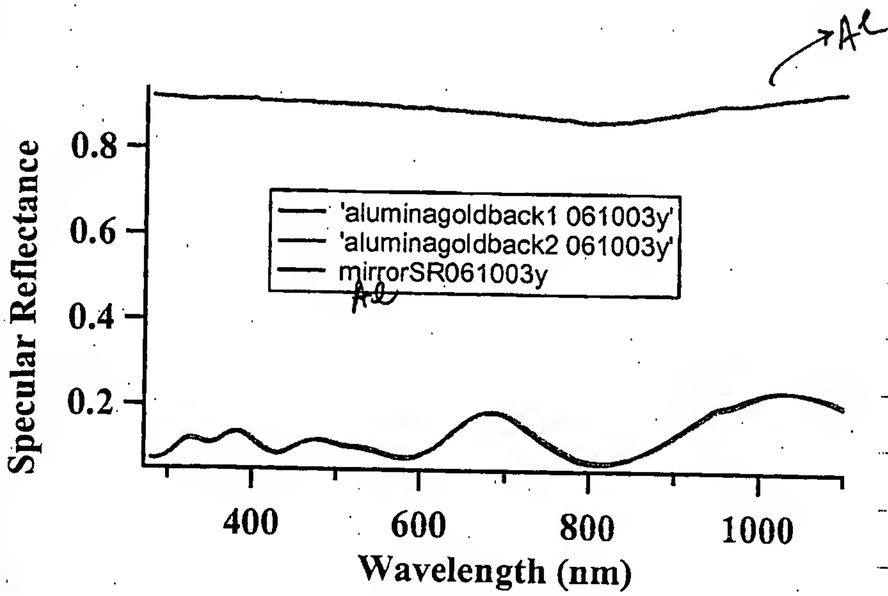


Entrance Slit - 1.25mm
Exit Apeture - 1.5mm

06/10/03

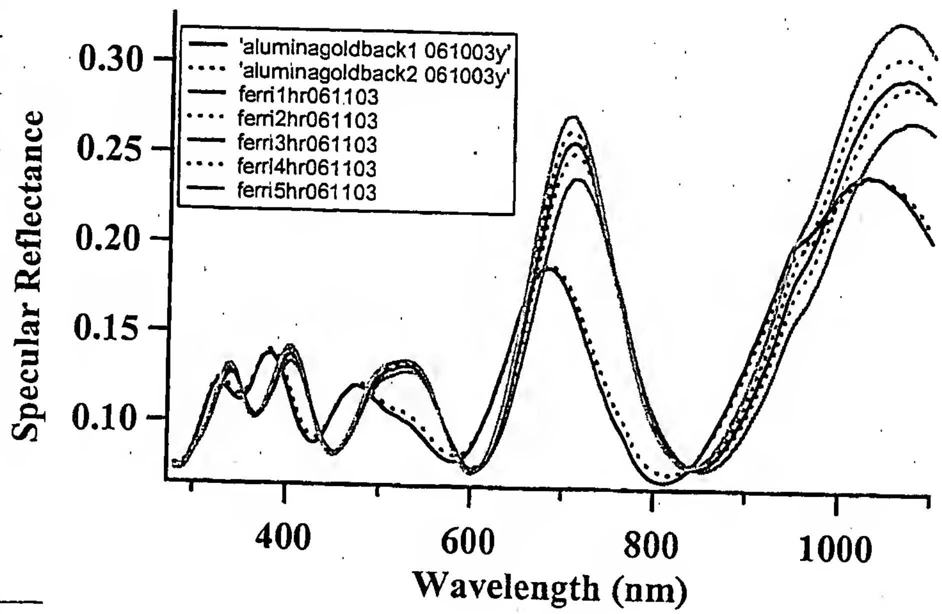


Two runs of dry slide coated with alumina/gold Shifting caused by cell movement.

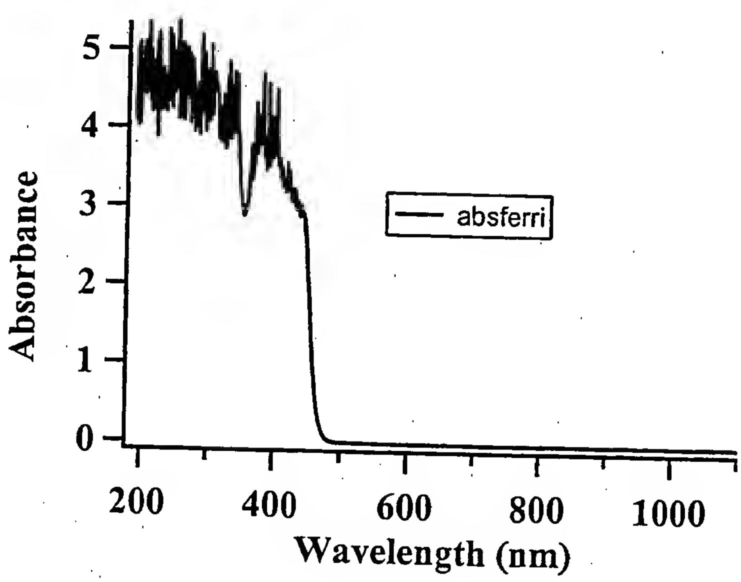


Superimposed Al SR and dry slide-alumina-gold

06/11/03

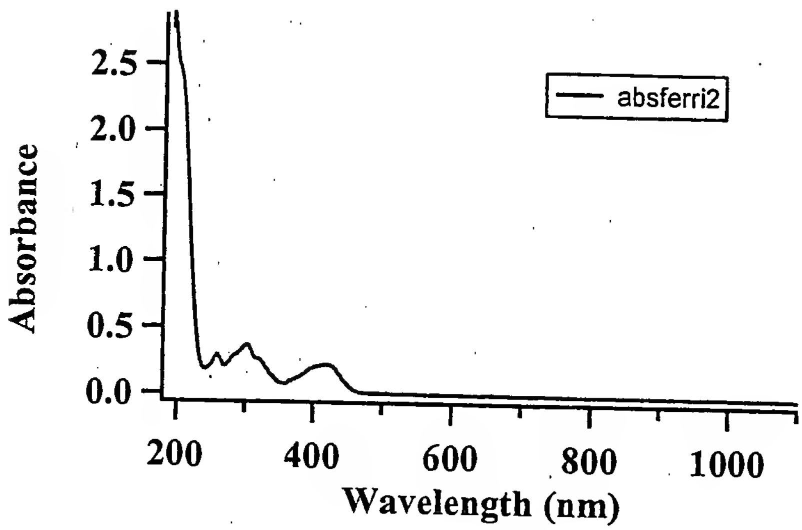


Alumina-gold back with ferricyanide over time 1hr, 2hr, 3hr, 4hr, 5hr
- Increase in intensity over time
- First shifting from blue to red



absorbance of 0.05M ferricyanide concentrated

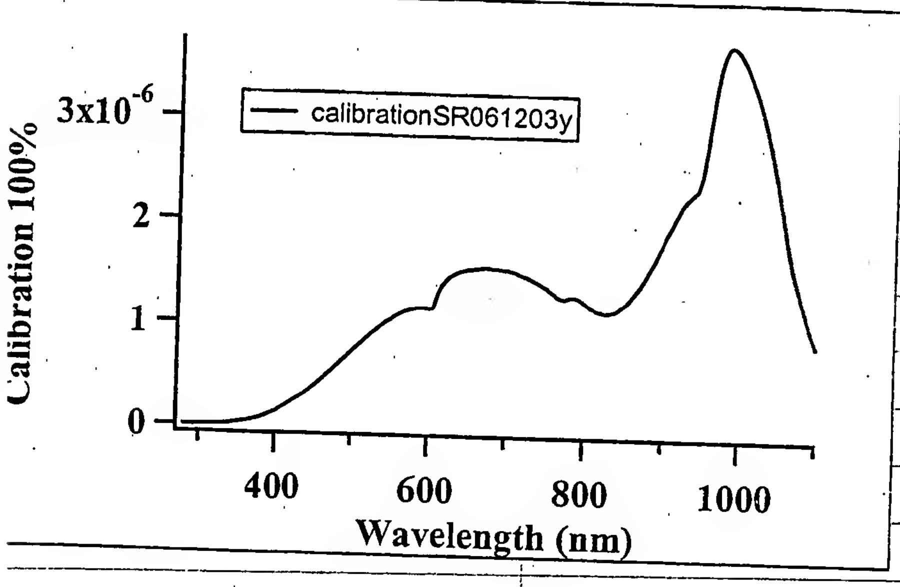
06/11/03



absorbance of dilute ferricyanide

06/12/03

Recalibration of system. 100% no reference sample



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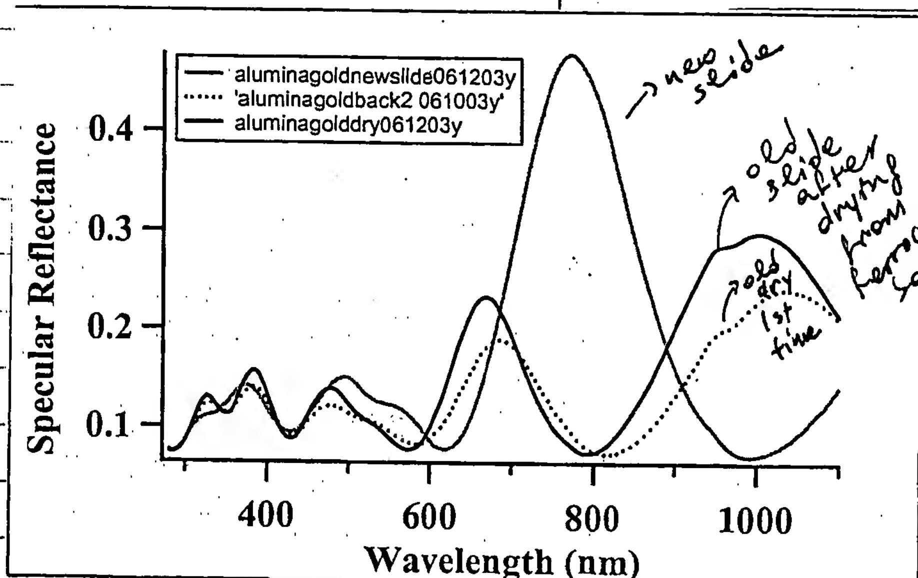
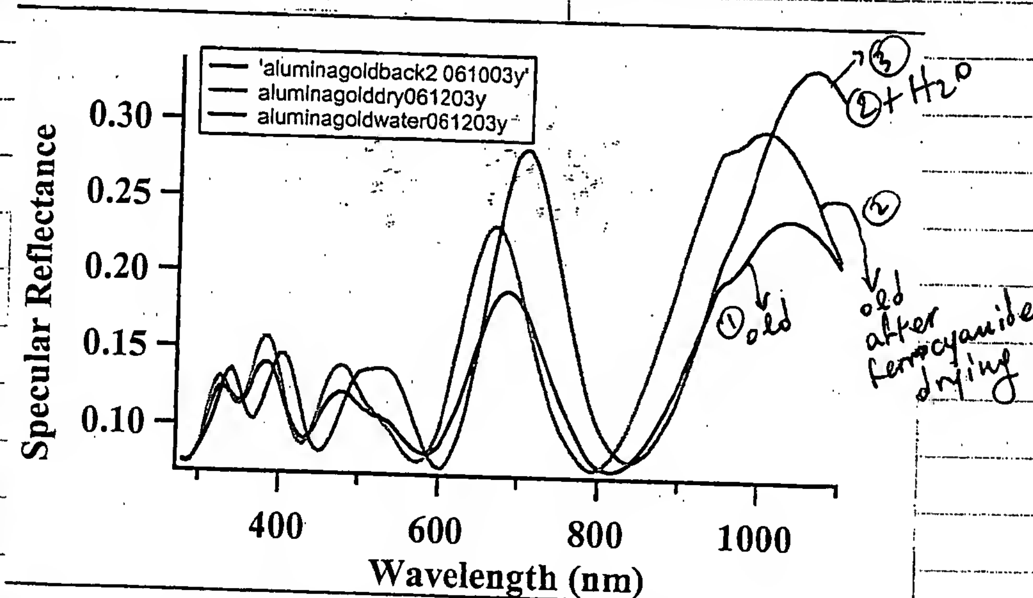


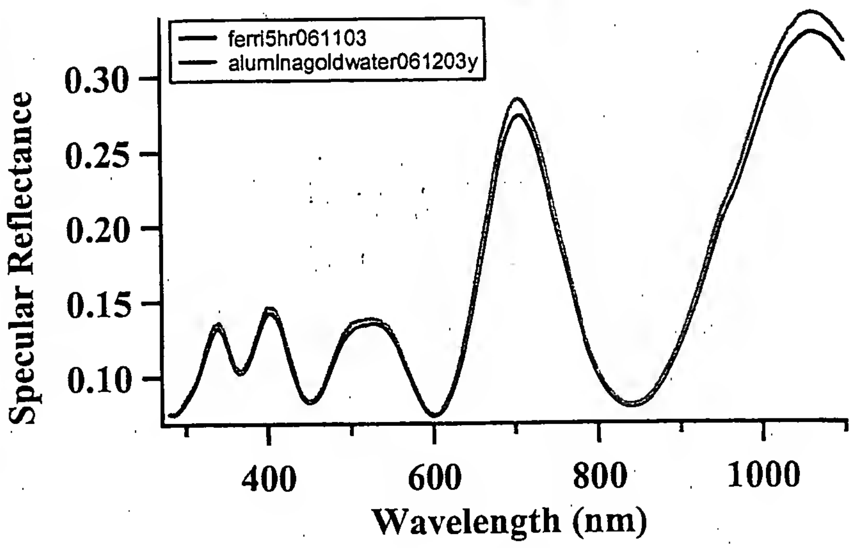
New slide had some similar features with old slide, however we observe a different spectrum.



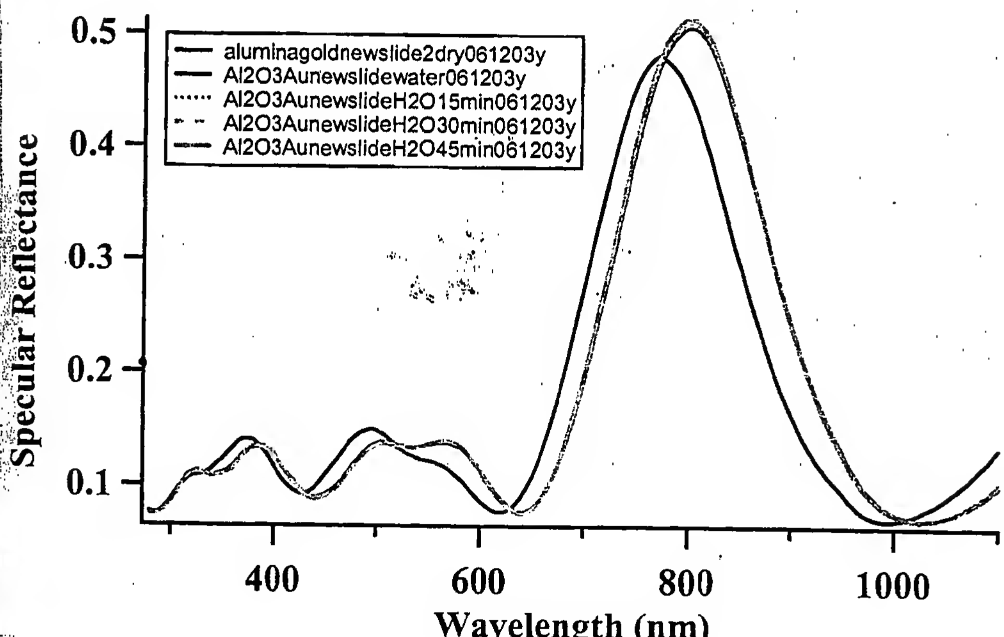
* It went back to the blue only shifted even further in the blue.

(solvent?)
H_2O is responsible for shifting and increasing of intensity.

06/12/03



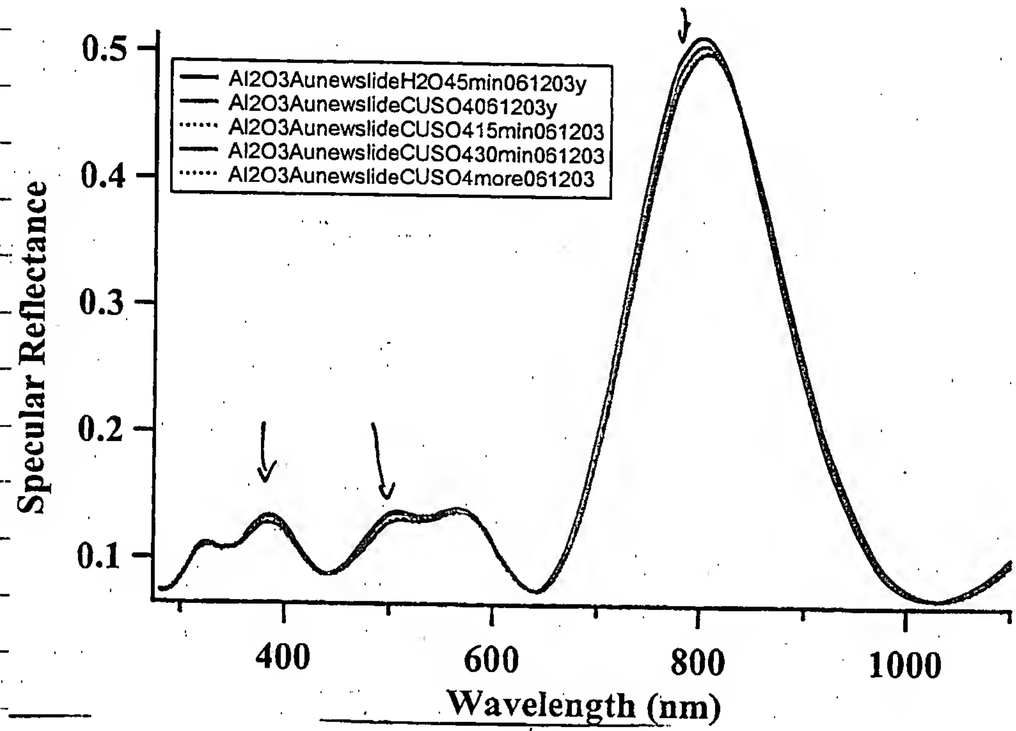
H_2O and ferrocyanide effect.



New slide and effect of H_2O over time.

No to much increase

06/12/03



We use $CuSO_4$ to see if we can spot any difference. Slight decrease of reflectance signal and red shifting is observed. (where the arrows are).

THE END

NEXT NOTEBOOK ⇒

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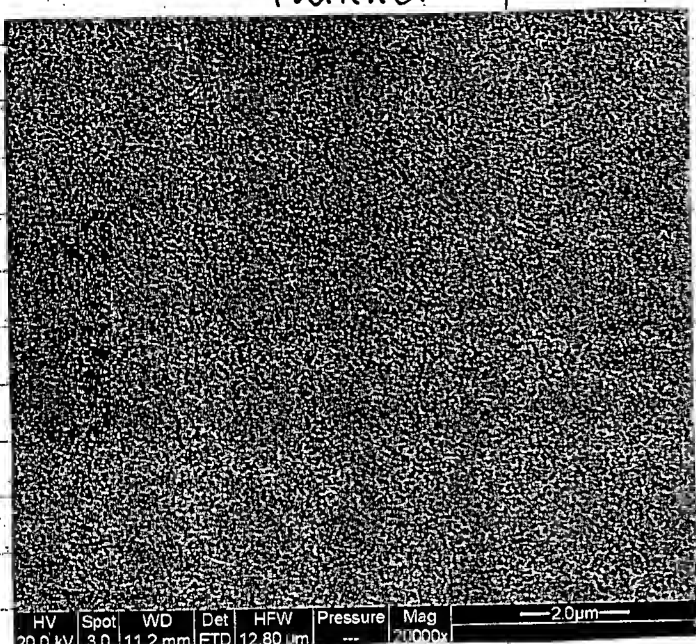
06/13/03

Performing SR experiments with Paul on alumina gold coated slides.

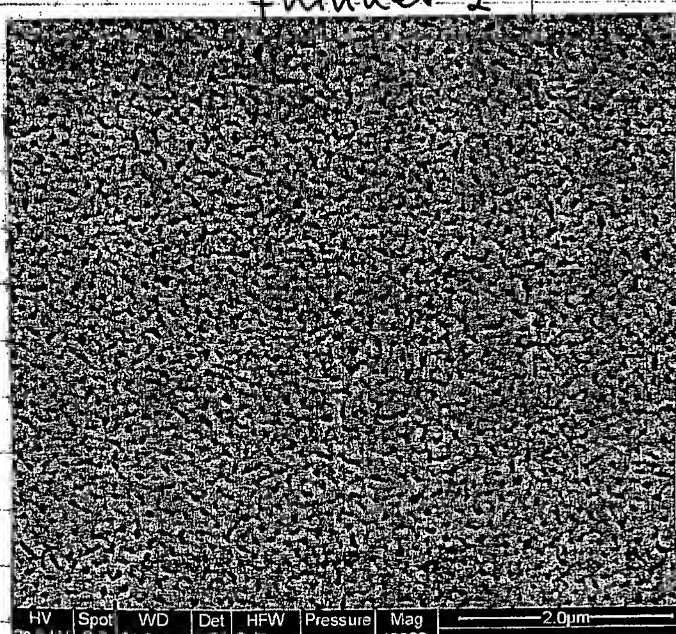
thinner 1



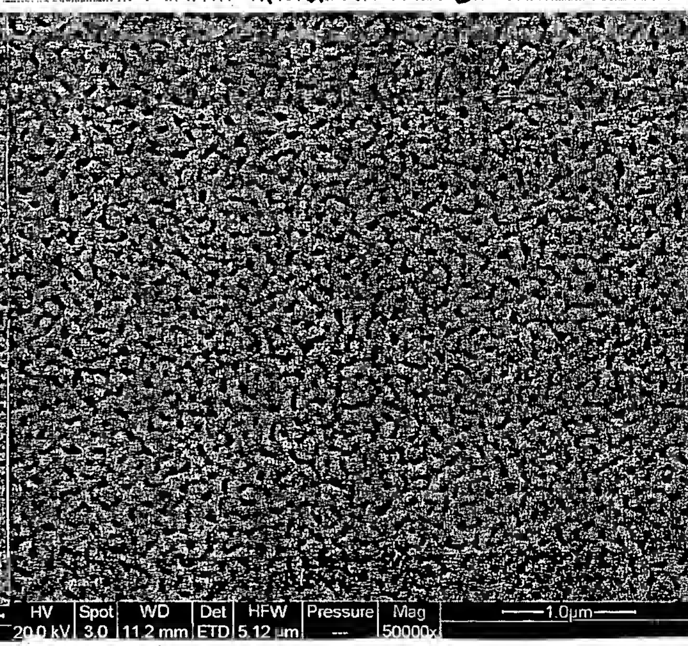
He coated some thinner (3.5 min) gold evaporation and some thicker (7 min) gold

SEM images of thinner coated Au ~ 100 nm show here over alumina from anodized Al slides.

thinner 2



thinner 3



Standard Al coating: (CVC-FTIR) 06/13/03

Al coated slides ~500nm P= 2000 W (Pinn+B)

Toggles = 8 Ar=16

(normal) tank

Presputter angle = 0 / Angle after toggles = 0

Manual presputtering = 30 min

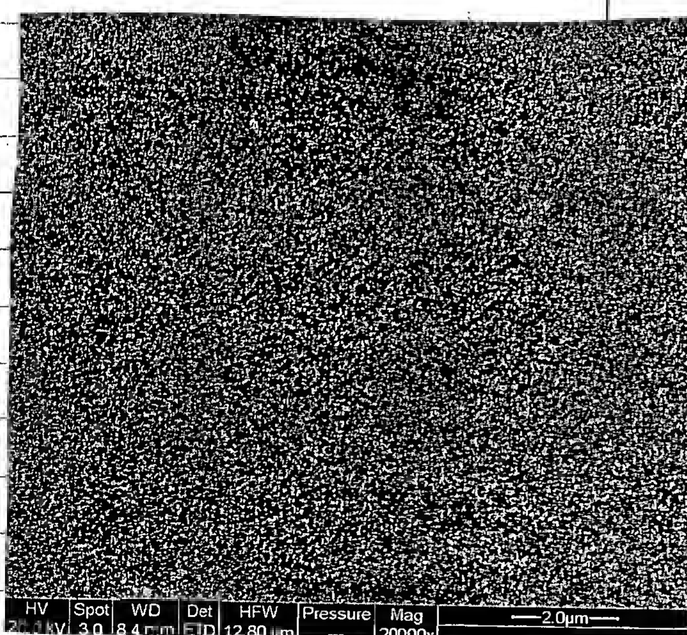
CW togglings

Start Angle = 25 Macro 2

Angle Width = 170

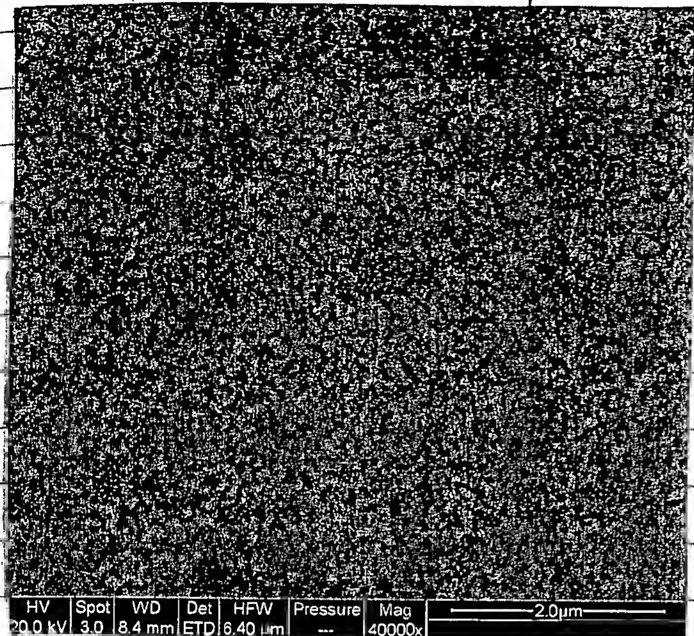
06/14/03

Thicker slides SEM images at spot size 2.0, 3.0

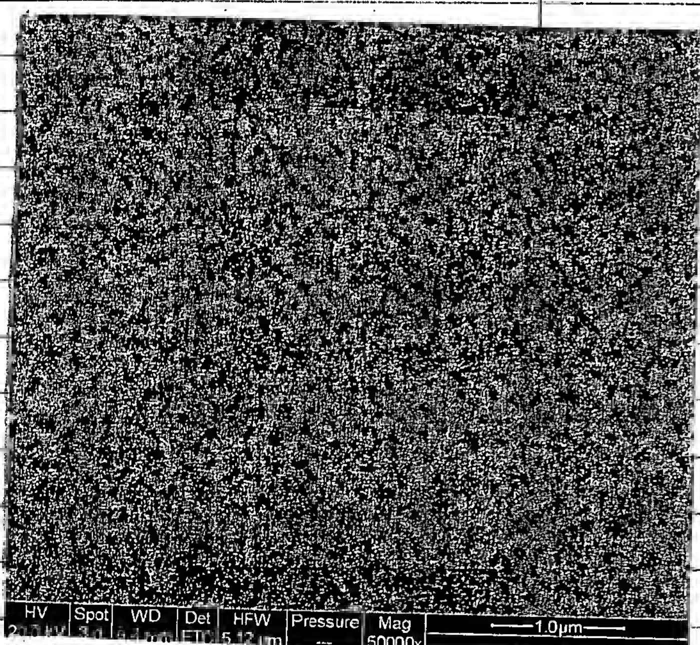


20,000x

06/14/03



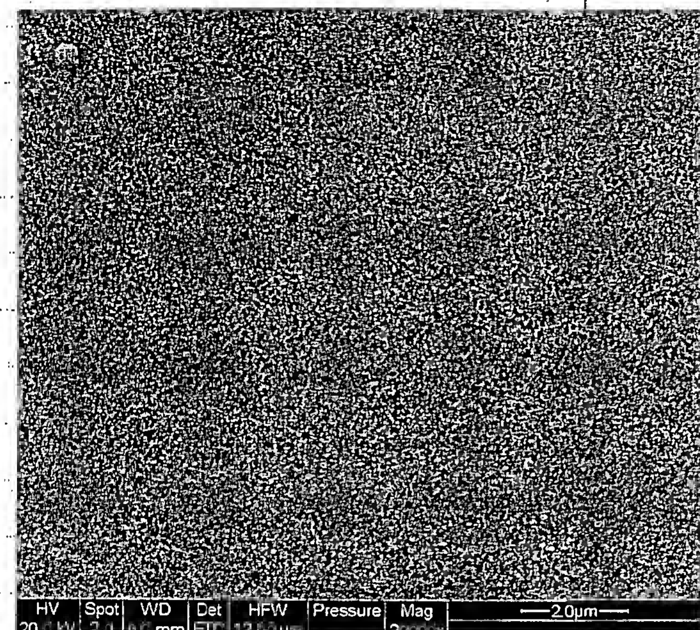
40,000x



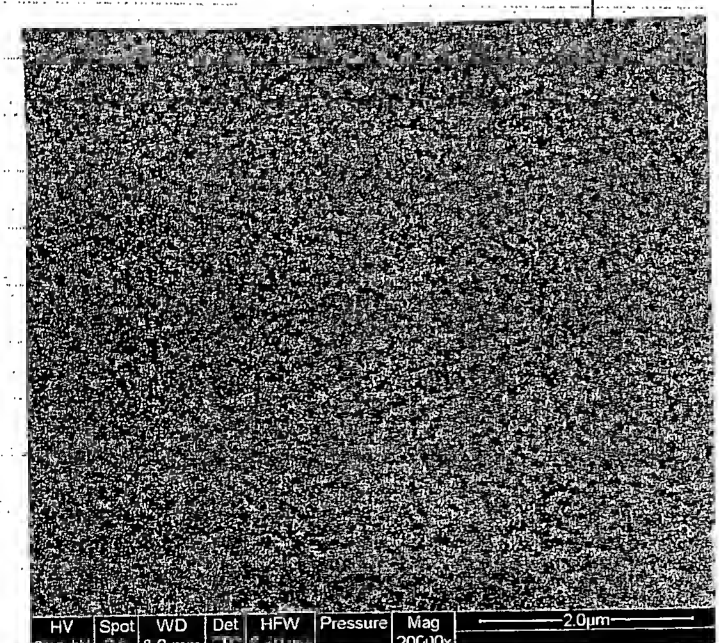
50,000x

8

06/14/03



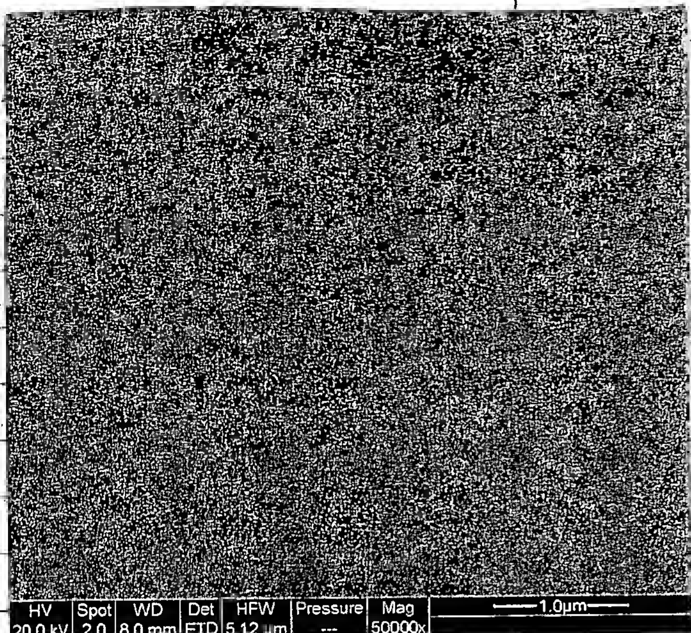
20,000x



40,000x

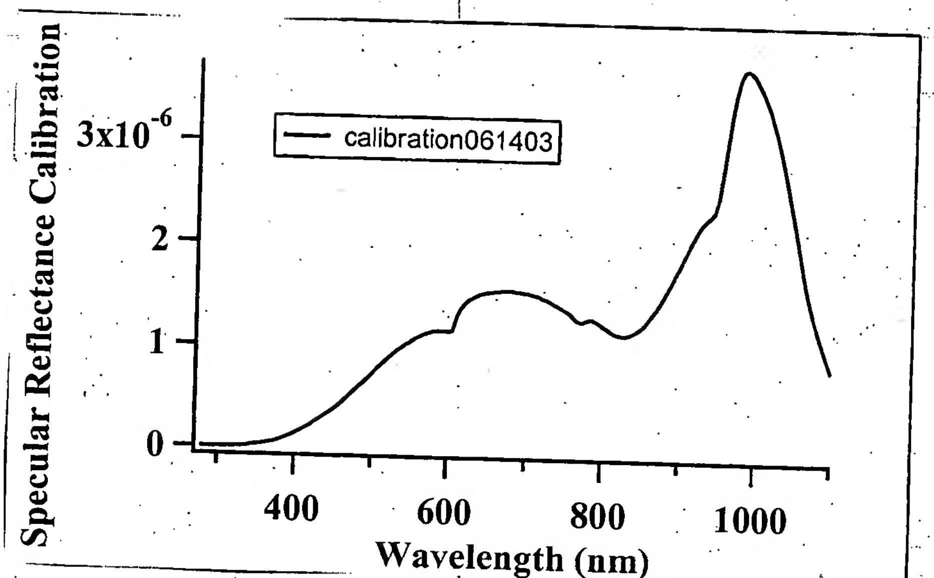
40,000x

06/14/03



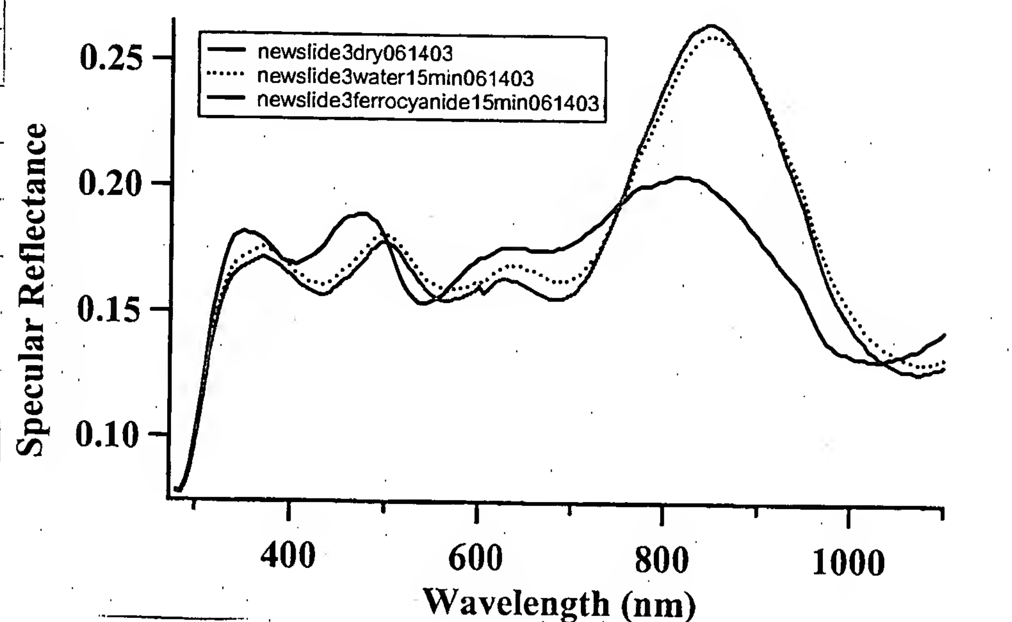
50,000x

06/14/03



of SR system

06/14/03



06/16/03

So far :
1) Thinner Au coating works better
2) From dry to wet we have a red shift and increase in intensity.
3) Slide from slide have different spectrum
4) Once the slide dried - second spectum blue shifted from original and dropped in intensity, but not as much as to meet the original intensity
5) H_2O and ferrocyanide solution cause the same effect (shift, intensity)

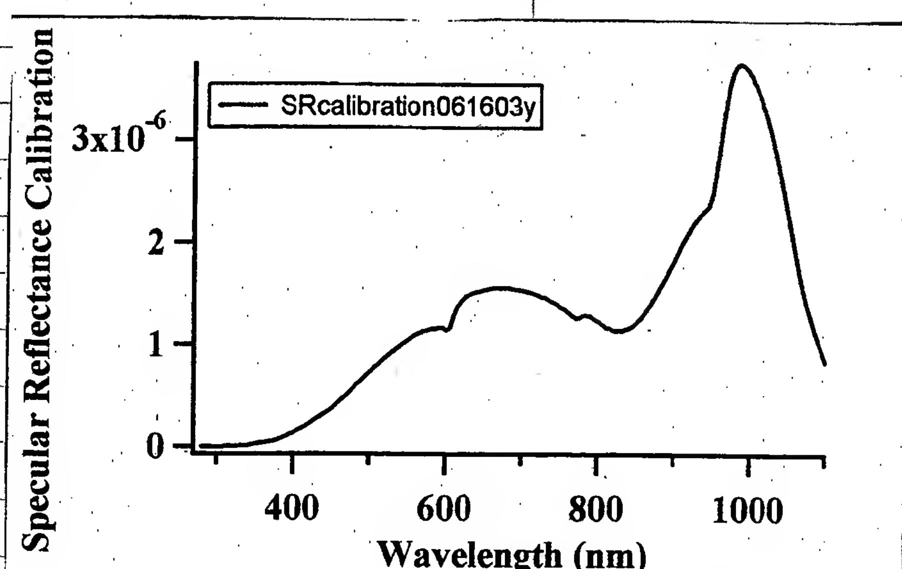
06/16/03

6) Over time blue shifting and increasing of intensity seems stronger for Ferrocyanide solution than H_2O (Need better H_2O controle/time)

7) $CuSO_4$ solution redshifted and lower intensity in the spectrum.

8) 061403 experiment showed:
H_2O -> red shift/increase of intensity
Ferrocyanide -> blue shift / increase of intensity in the red region / decrease of intensity in the blue region

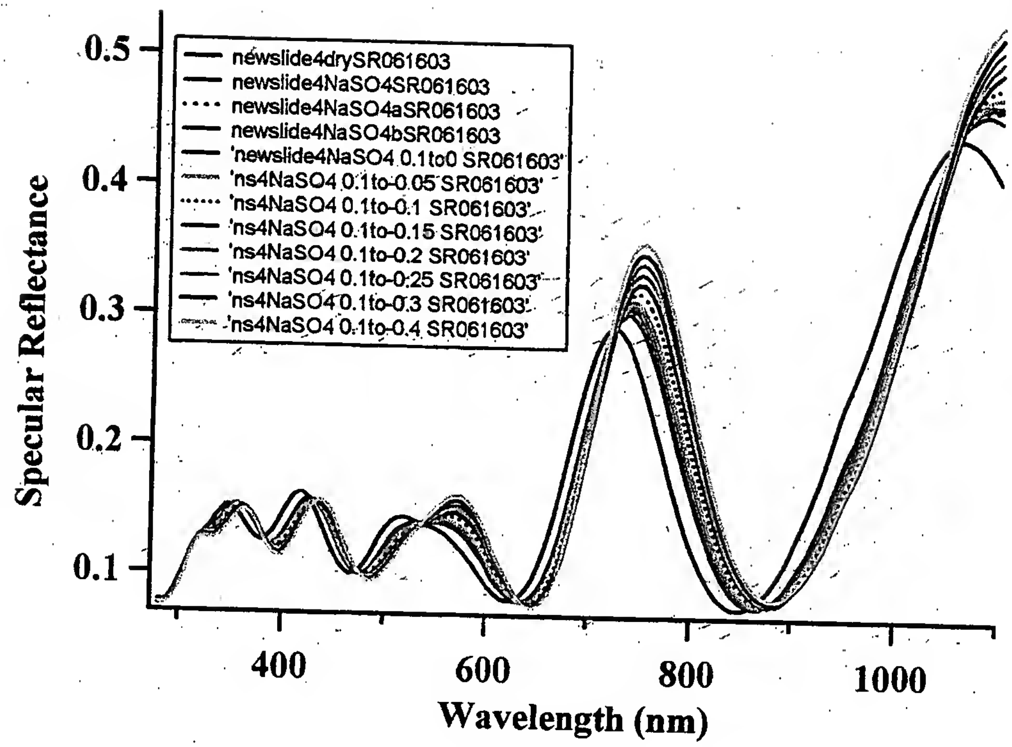
06/16/03



Experiments with combination of spectroscopy and electro-chemistry

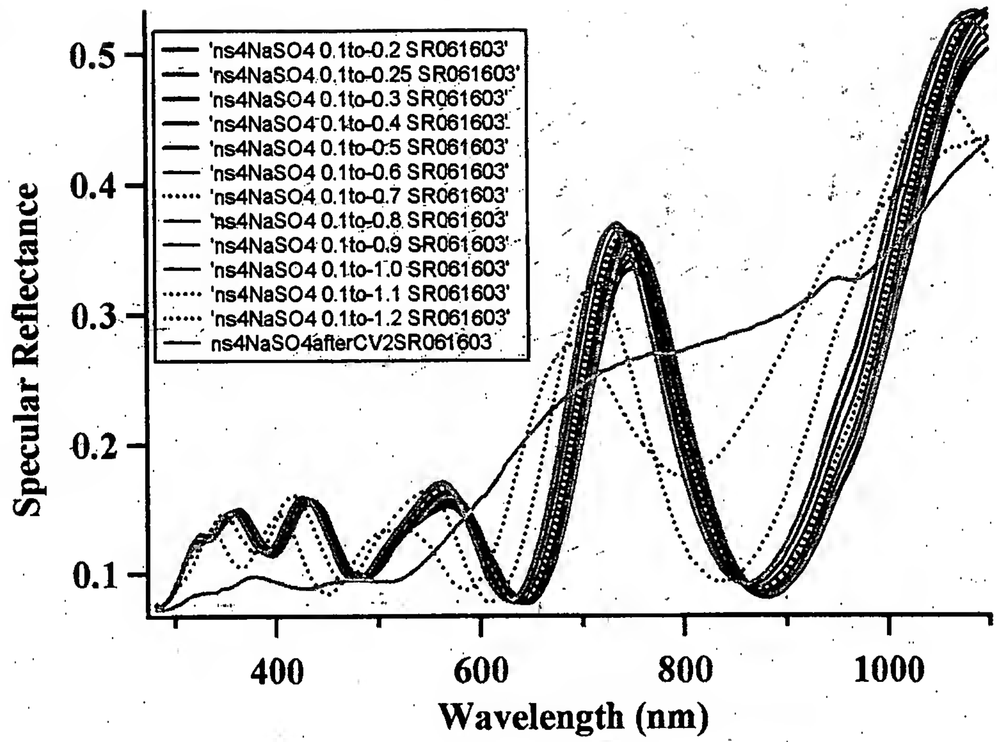
Calibration against 100% / No reference sample
Same system as before.

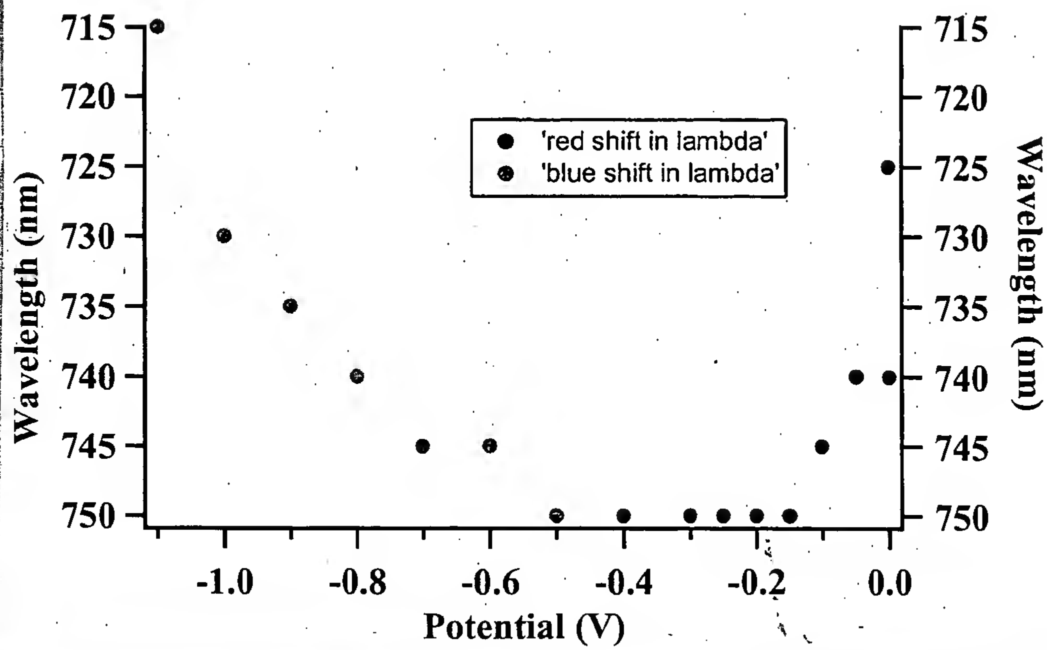
06/16/03



From dry alumine/gold (3.5min) thinner slide (SEM) to wet with $NaSO_4$ solution and applied different steady potential. We see red shifting and increase of intensity at 725nm and 1060nm. Red shifting and increase of intensity at 520nm. Also oberve the isosbestic point and increase of a different peak at 570 nm.
Peaks at 350nm and 420 nm show red shifting but no increase, rather a slight decrease of intensity.
Peak at 320 nm does not change.

06/16/03

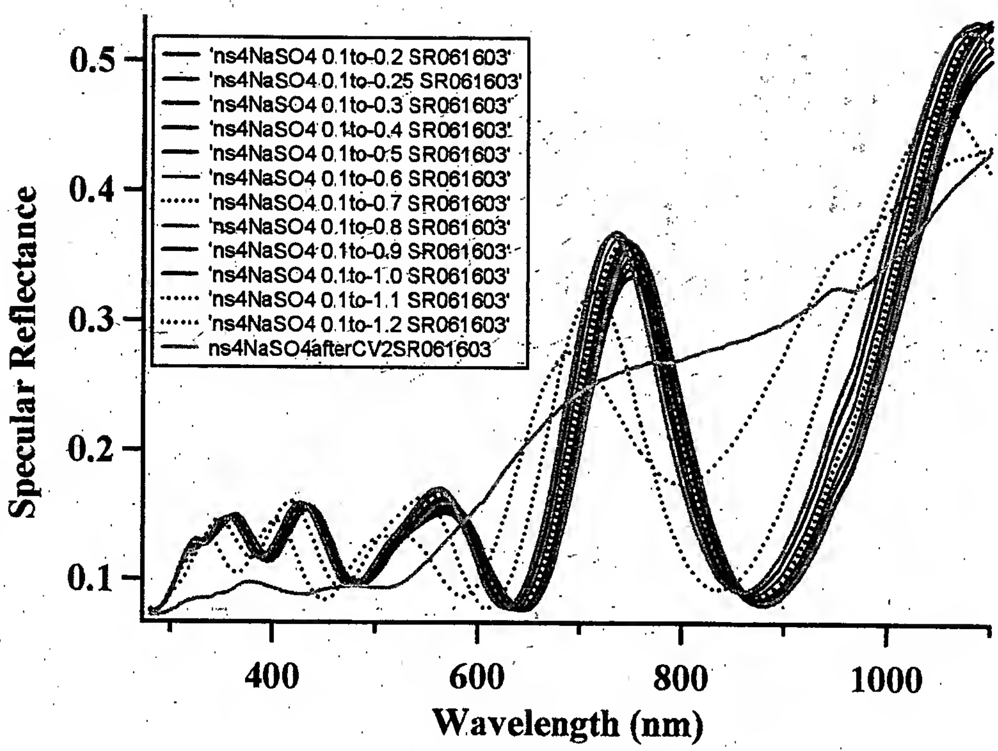


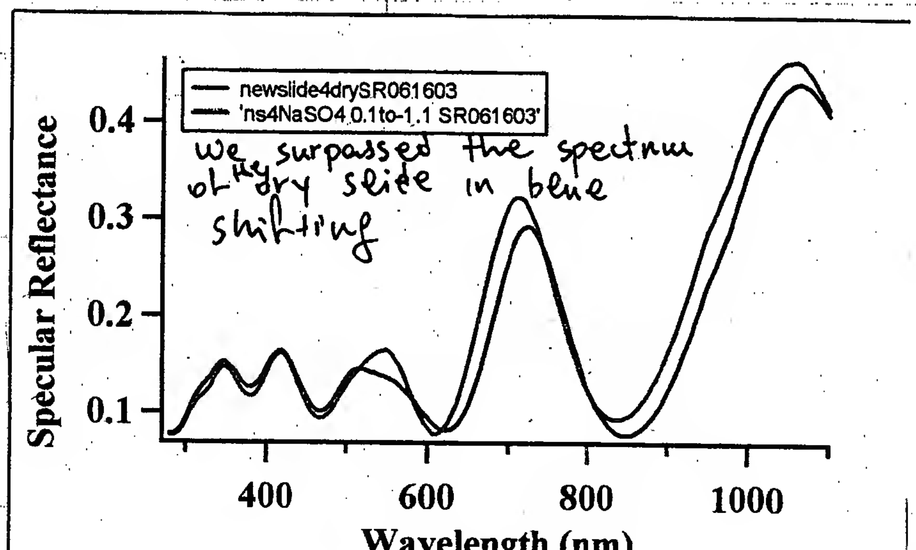


NaSO4 0.05M ?

-(V) her pores

06/16/03





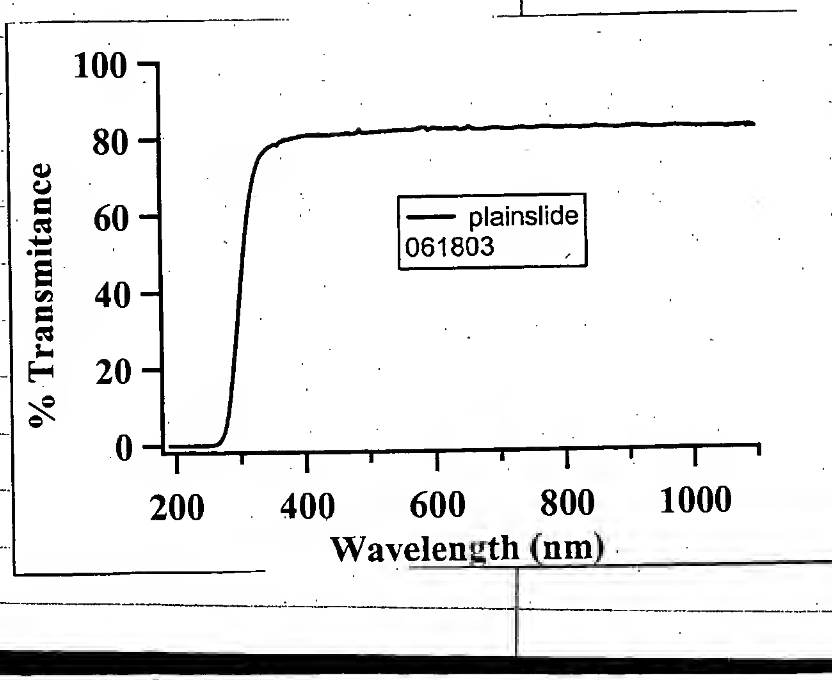
$NaSO_4$ 0.05M

Application of stepping potential (V) for H_2 evolution in the alumine pores

06/16/03

As the potential reaches −0.2 we observe a blue shifting (slight) and increase of intensity in ~1060nm, 725nm, 570nm, but no increase of intensity at 420nm and 350nm. No shifting at 320nm but decrease in intensity. At −1.1 we have great H_2 evolution, great blue shift and decrease of intensity in all peaks.
At −1.2 more blue shifting and lower intensity however, the spectrum has changed, indication that there is something wrong with the film (delamination) (flaking of Al_2O_3/Au)
After the second cyclic voltametric the spectrum is almost completely altered.

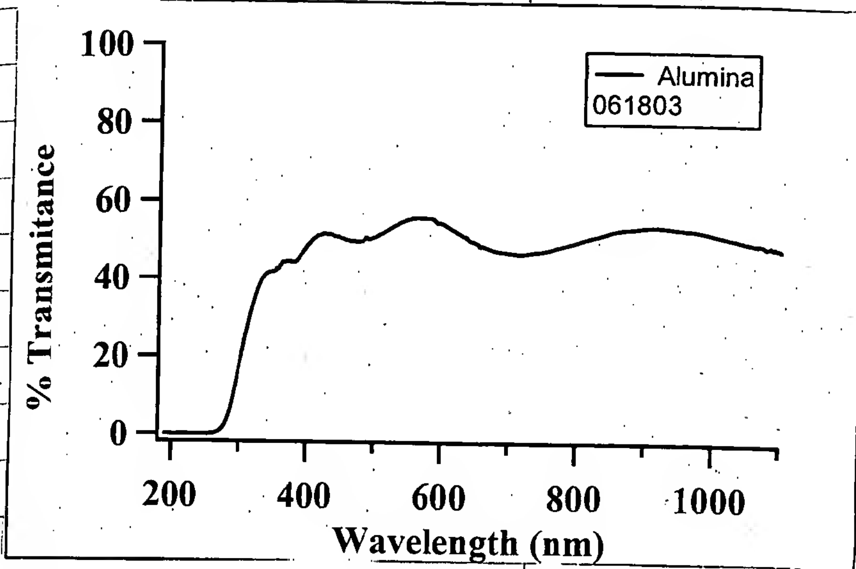
06/18/03



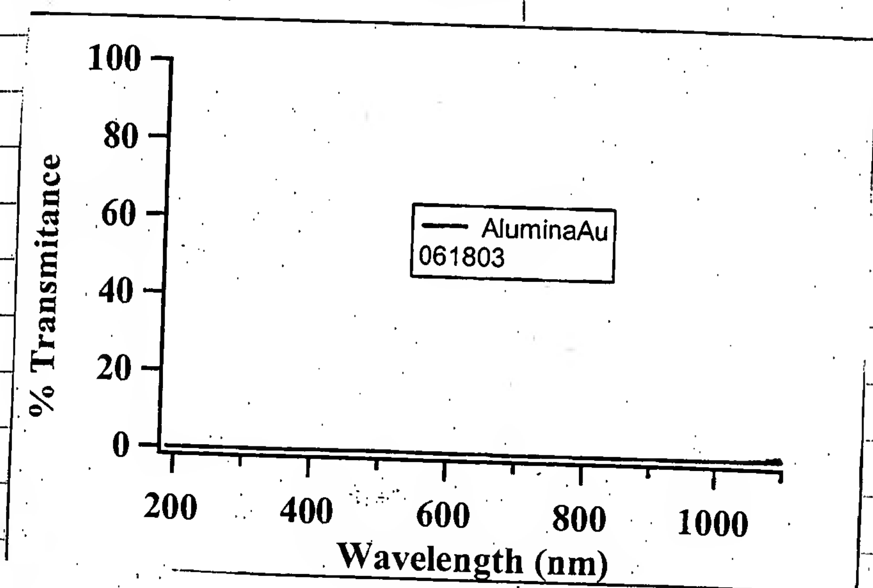
positioned at 45°

Used UV-vis in P. Chem. lab

06/18/03

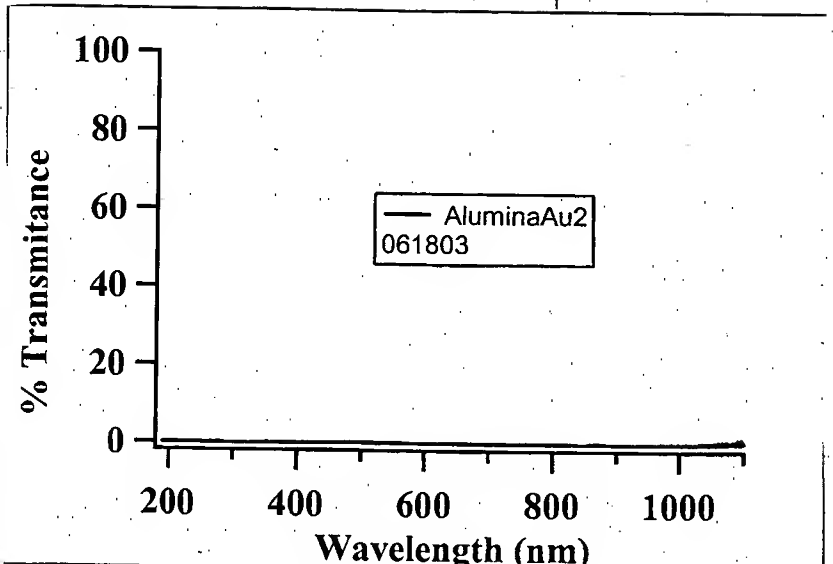


potitioned at 45°



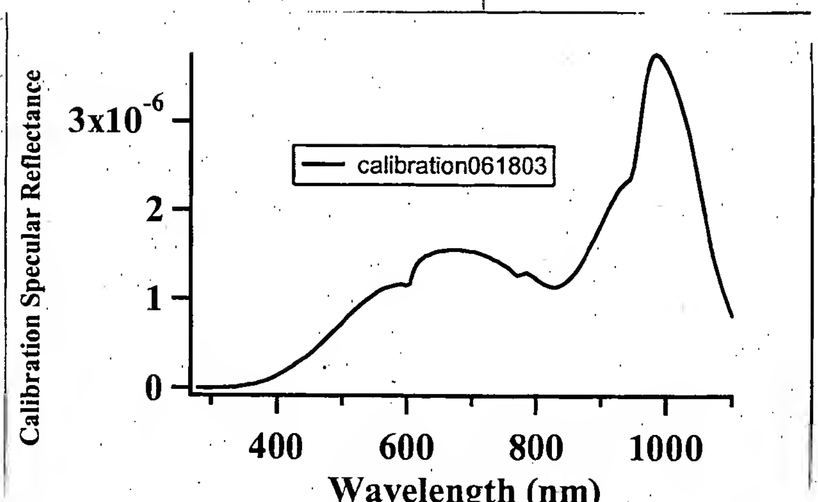
positioned at 45°

06/18/03



positioned at 45°

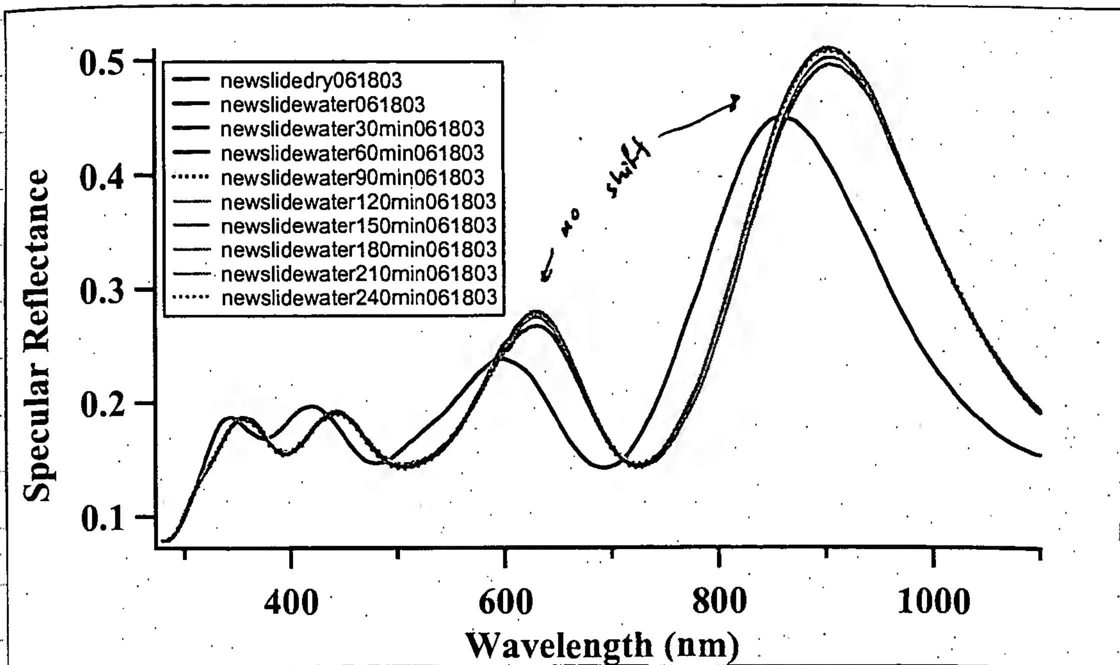
06/18/03



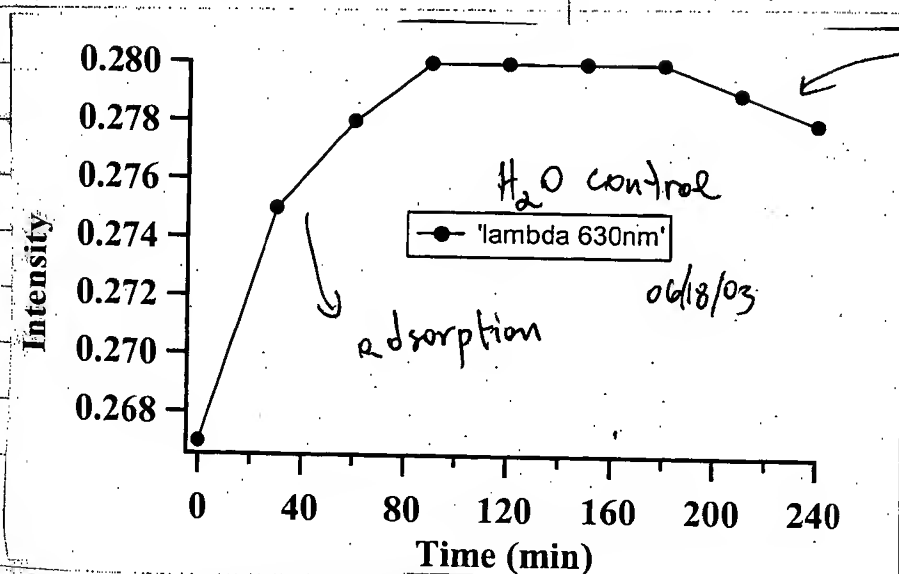
Water monitoring over time of 4 hrs every 30 min. Gold coated slide over alumina positioned at 45° and detector at 90°.

Same setup as before.

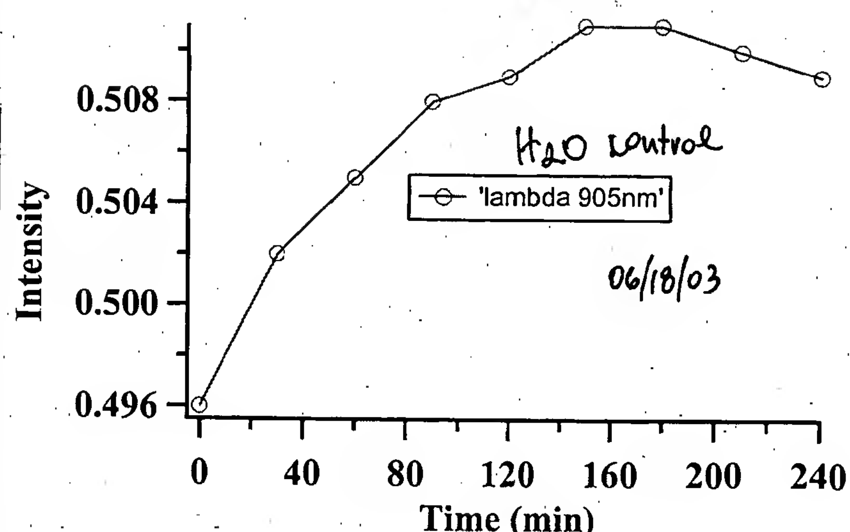
06/18/03



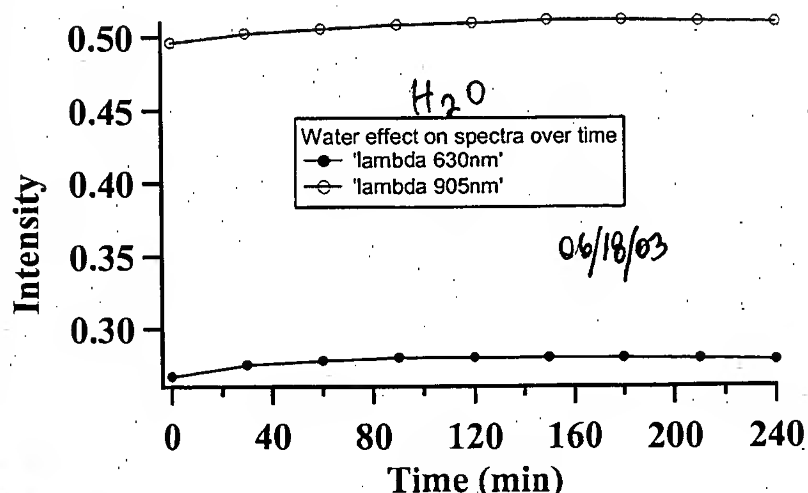
No observed shifting, small increase in intensity. Peaks before 500nm do not change



06/18/03

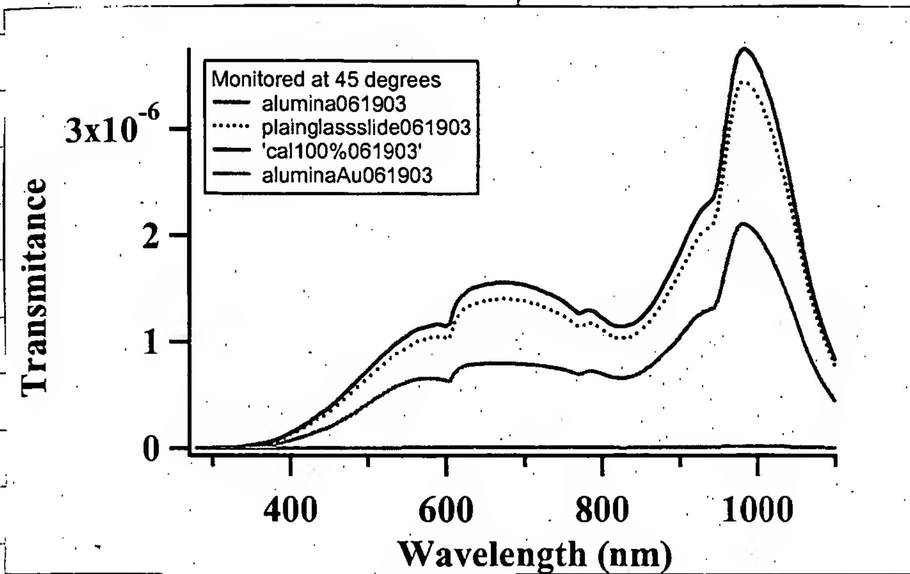


Intensity
0.496
0.500
0.504
0.508
0
40
80
120
160
200
240
Time (min)
'lambda 905nm'
H2O control
06/18/03

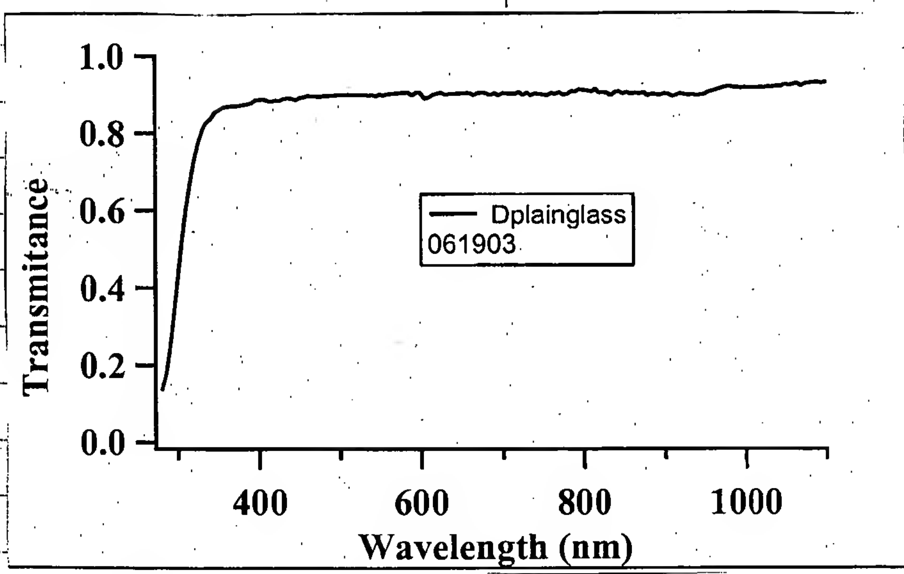


Intensity
0.30
0.35
0.40
0.45
0.50
0
40
80
120
160
200
240
Time (min)
H2O
Water effect on spectra over time
'lambda 630nm'
'lambda 905nm'
06/18/03

06/19/03



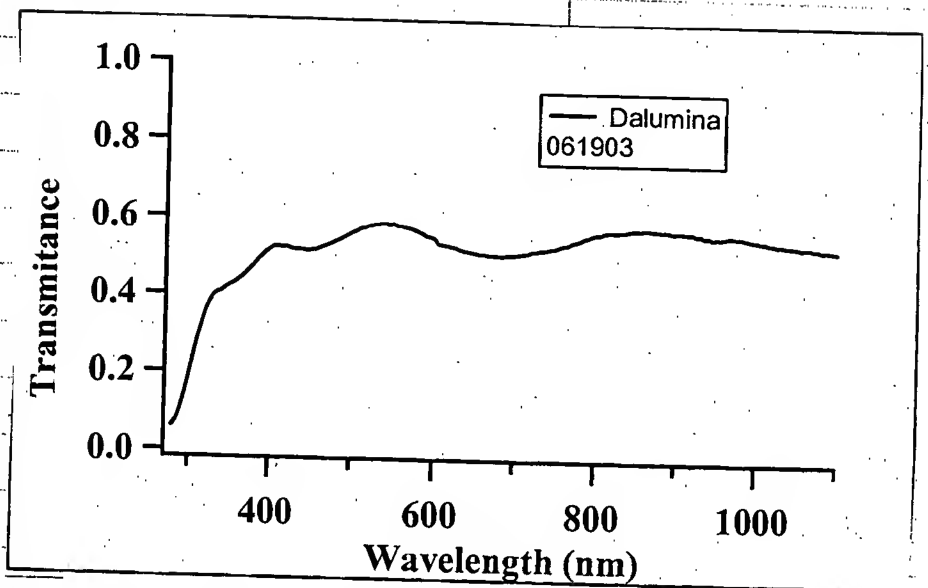
Using the same setup as SR goniospectrometer I measured
1) cal 100%
2) plain slide
3) slide + alumina
4) slide + alumina + Au
at 45° degrees



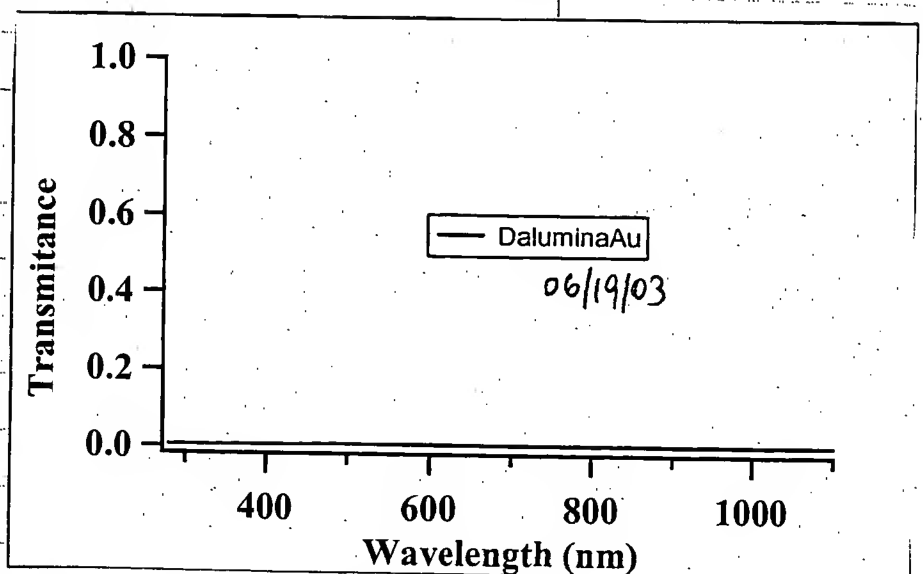
Slit : 1.25 mm, 1.5 mm ↔ apeture.
W / Si

D: divided by calibration.

06/19/03

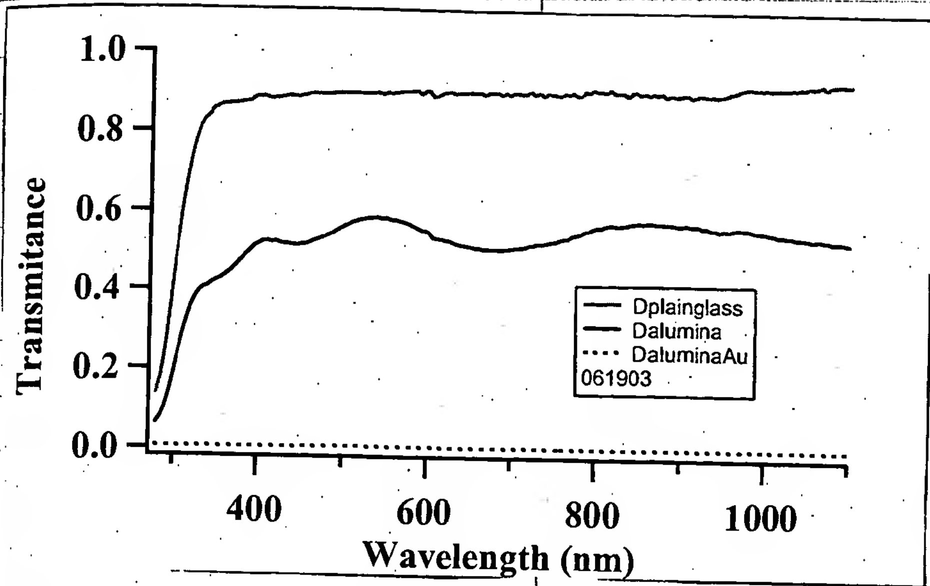


at 45°



at 45°

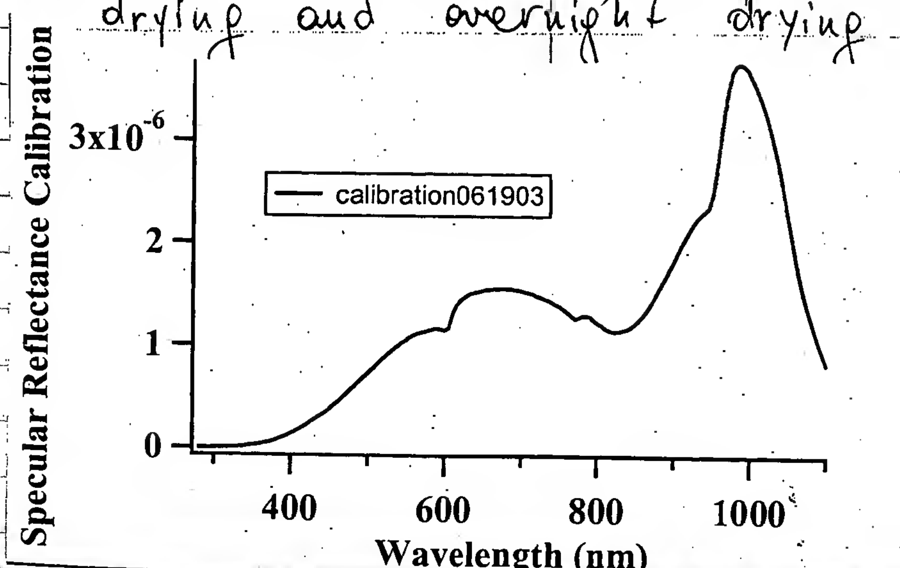
06/19/03



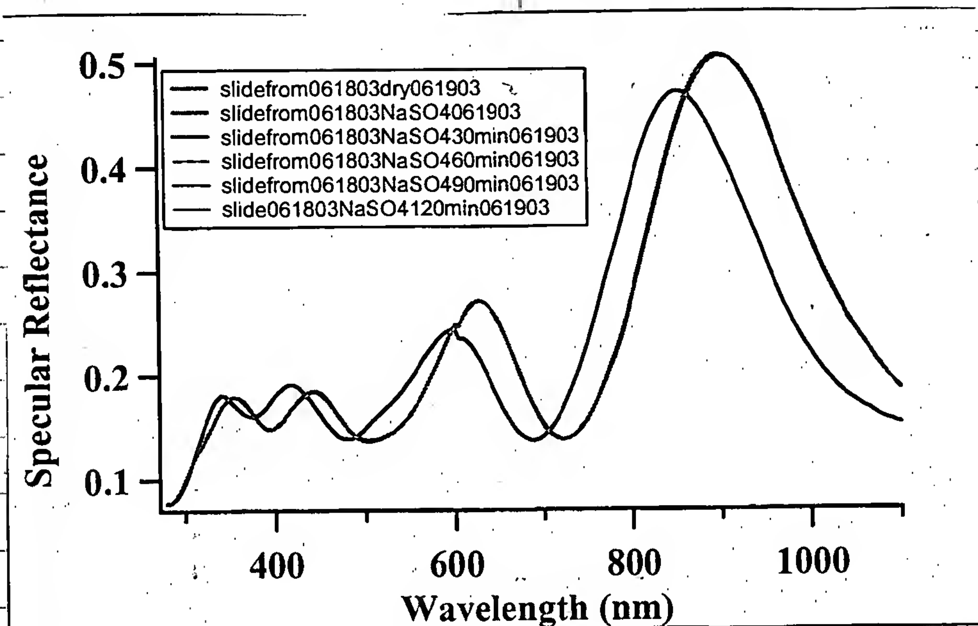
at 45°

I also run Na_2SO_4 (0.05M) solution in the cell over time. Slide used was the same as the one used for H_2O monitoring over time 06/18/03

* H_2O may have still be in pores after N_2 drying and overnight drying at room T.



06/19/03

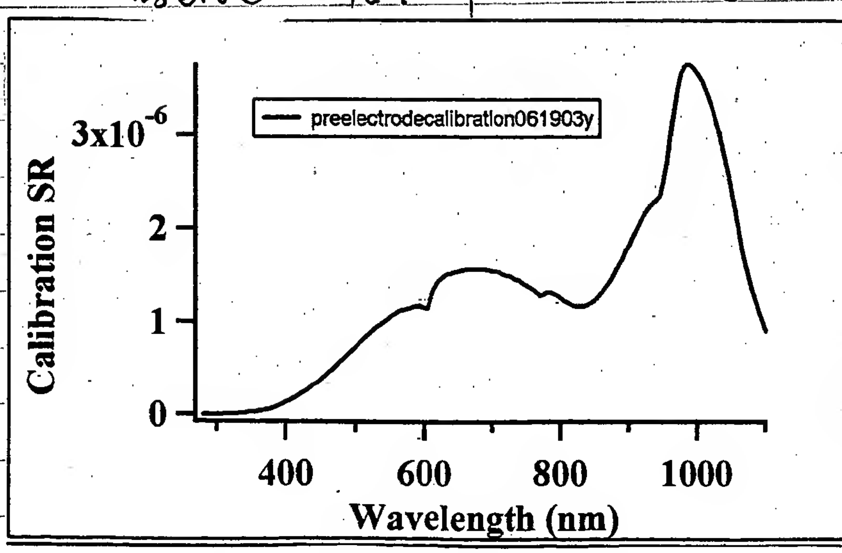


No change in the slide + H_2O

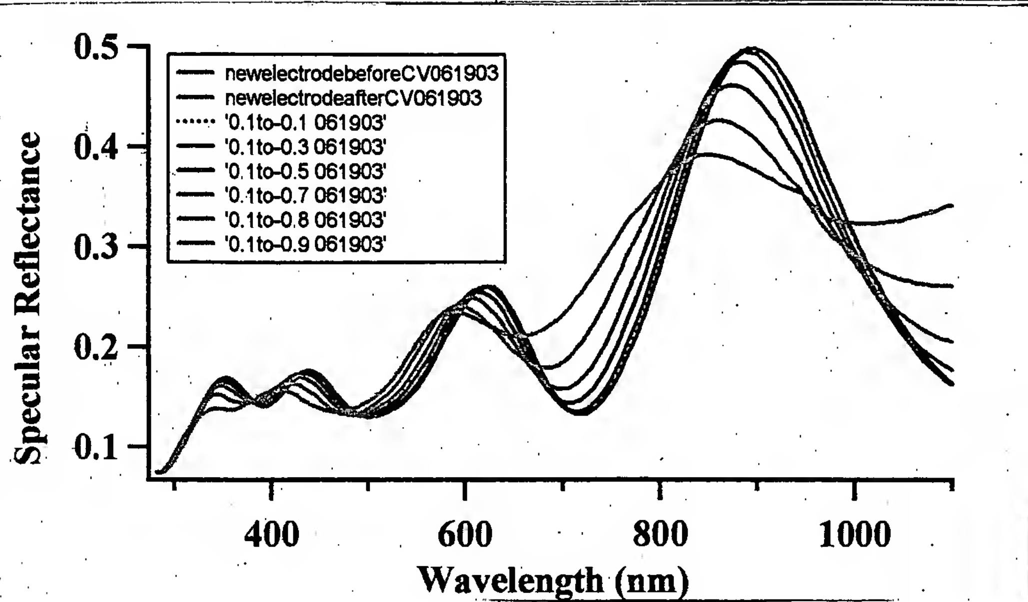
just initial increase and red shift.

The same slide as above we used to do electrochemical study 06/19/03

We observe a ~45nm shift (red and blue)

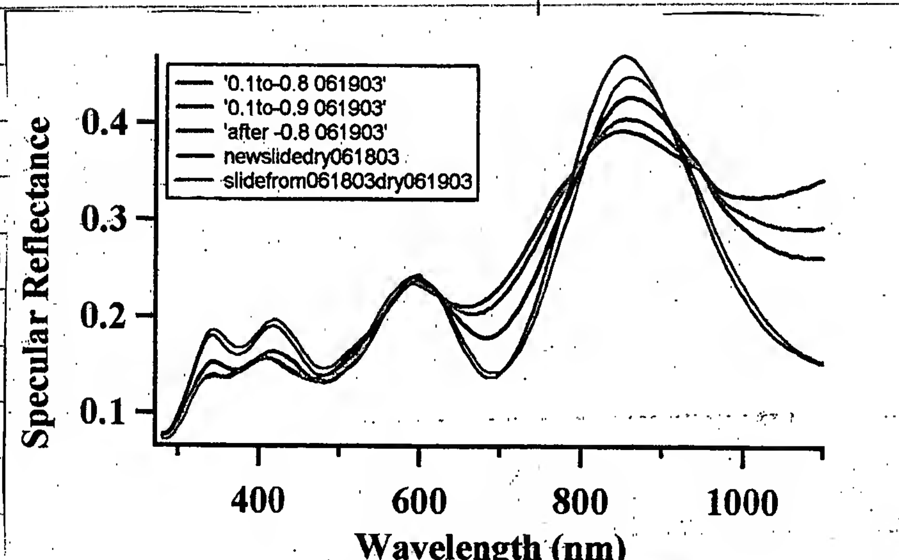


06/19/03

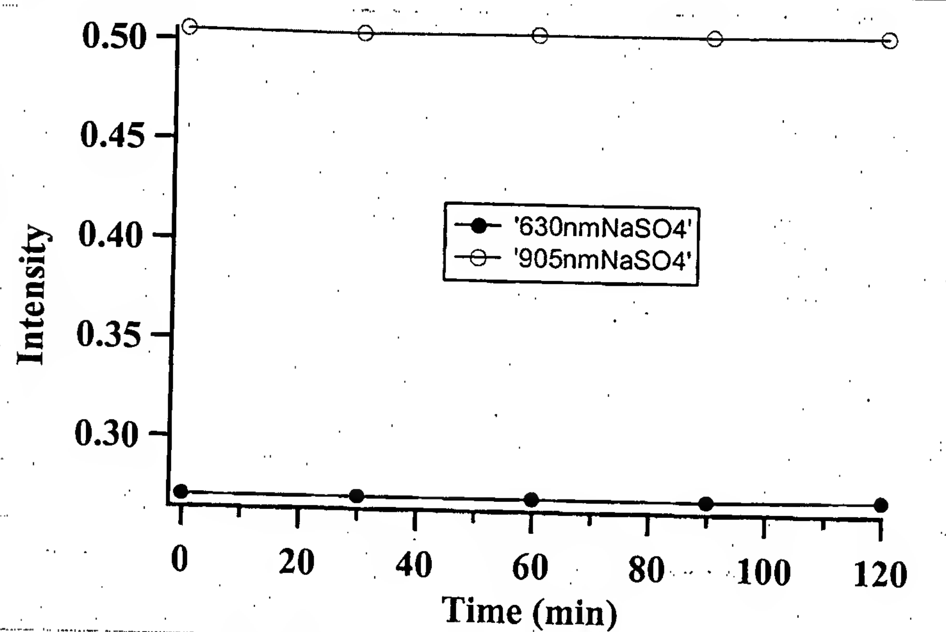


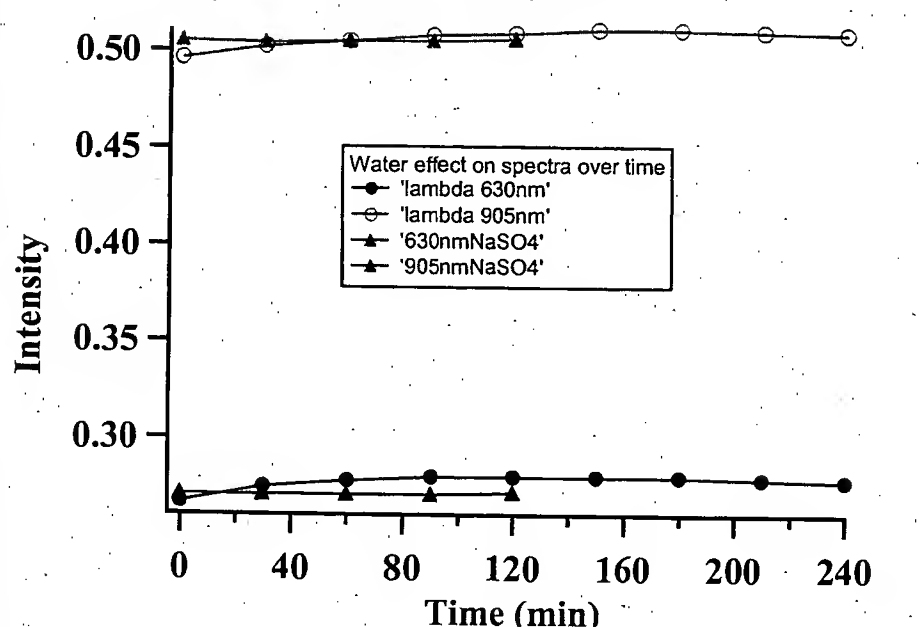
06/20/03

we observe

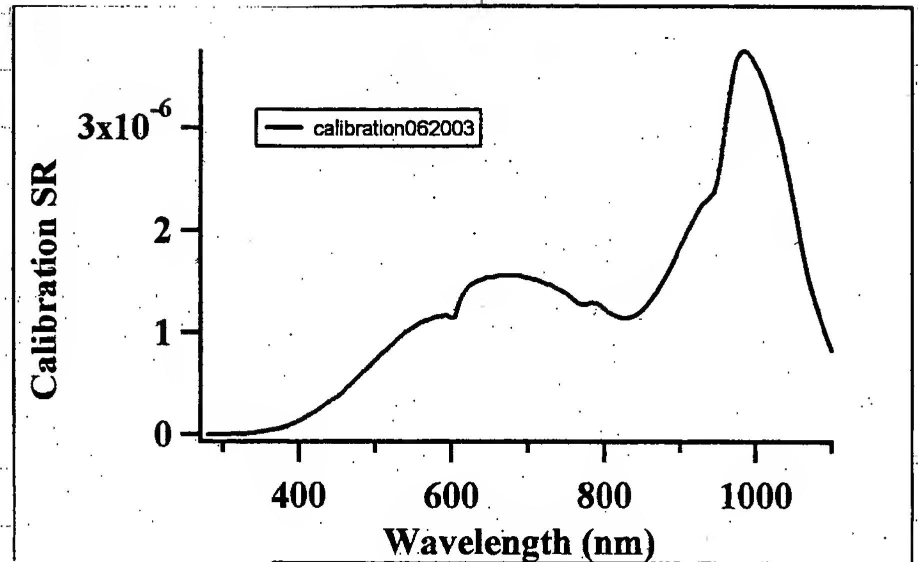


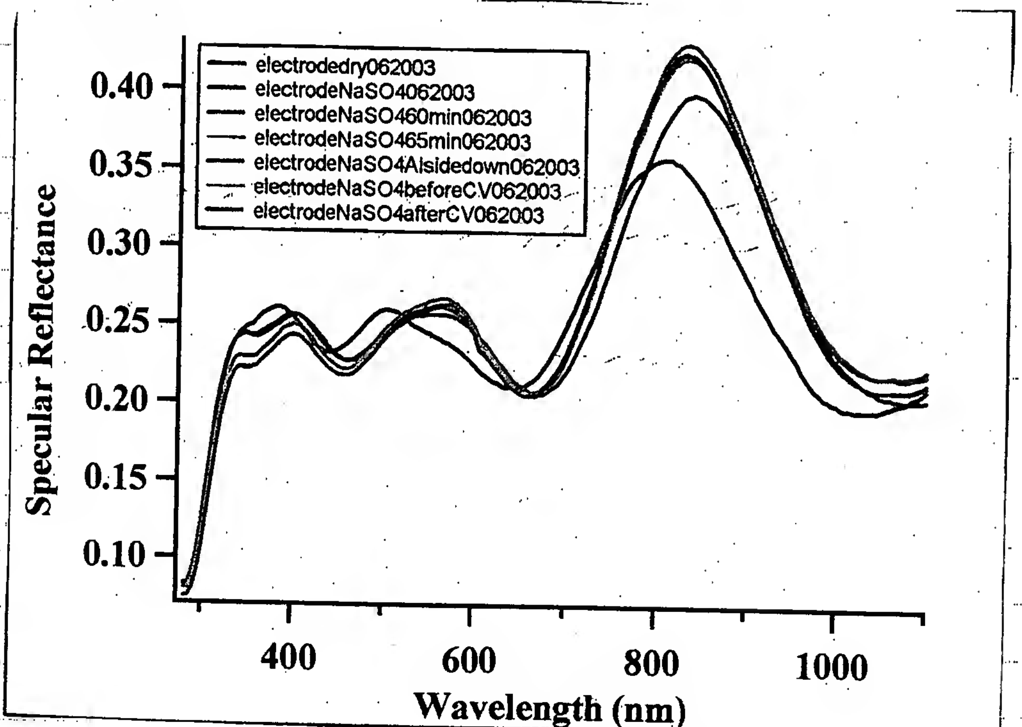
06/20/03


0.50
0.45
0.40
0.35
0.30
Intensity
'630nmNaSO4'
'905nmNaSO4'
0
20
40
60
80
100
120
Time (min)

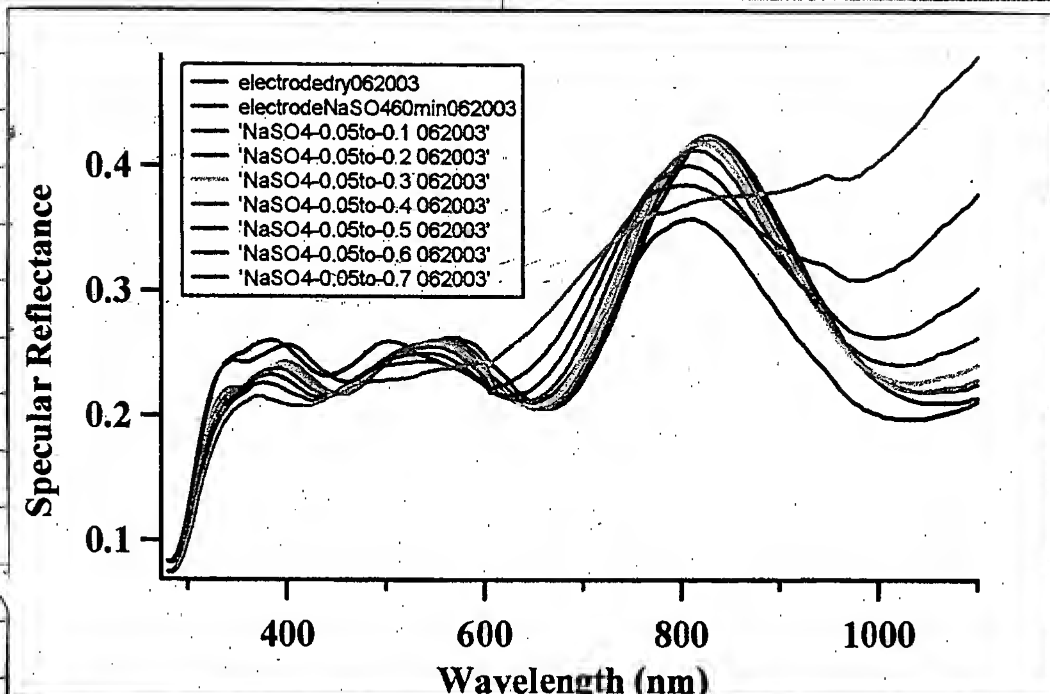

0.50
0.45
0.40
0.35
0.30
Intensity
Water effect on spectra over time
'lambda 630nm'
'lambda 905nm'
'630nmNaSO4'
'905nmNaSO4'
0
40
80
120
160
200
240
Time (min)

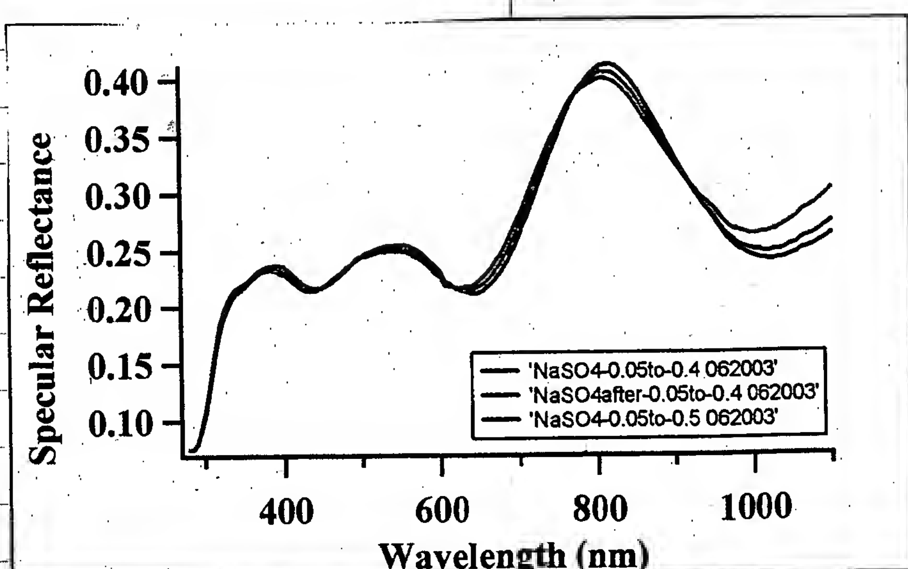
06/20/03


calibration062003
Calibration SR
3x10^-6
2
1
0
400
600
800
1000
Wavelength (nm)


electrodedry062003
electrodeNaSO4062003
electrodeNaSO460min062003
electrodeNaSO465min062003
electrodeNaSO4Alsidedown062003
electrodeNaSO4beforeCV062003
electrodeNaSO4afterCV062003
Specular Reflectance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
400
600
800
1000
Wavelength (nm)

06/20/03


electrodedry062003
electrodeNaSO460min062003
'NaSO4-0.05to-0.1 062003'
'NaSO4-0.05to-0.2 062003'
'NaSO4-0.05to-0.3 062003'
'NaSO4-0.05to-0.4 062003'
'NaSO4-0.05to-0.5 062003'
'NaSO4-0.05to-0.6 062003'
'NaSO4-0.05to-0.7 062003'
Specular Reflectance
0.4
0.3
0.2
0.1
400
600
800
1000
Wavelength (nm)


0.40
0.35
0.30
0.25
0.20
0.15
0.10
Specular Reflectance
'NaSO4-0.05to-0.4 062003'
'NaSO4after-0.05to-0.4 062003'
'NaSO4-0.05to-0.5 062003'
400
600
800
1000
Wavelength (nm)